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TRW, Inc.
Redondo Beach, CA

Prepared for

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The report gives results of a comprehensive multimedia emissions assessment of the cyclone-fired La Cygne No. 1 boiler, equipped with SO2 and particulate emission controls. Levels 1 and 2 procedures were used to characterize pollutant emissions in gaseous, liquid, and solid process streams. Assessment results, in conjunction with assumed typical and worst case meteorological conditions, were used to estimate the environmental impact of emissions from this type of unit. Principal conclusions were: (1) The risk of violating NAAQS for 24 hour and annual average levels is low; however, units using high sulfur fuel may exceed short term NAAQS for SO2. (2) Little adverse health effect is anticipated as a result of SO2, SO4 (--), and particulate emissions projected from widespread use of coal-fired units of the type tested. (3) Increases in the concentrations of Cd and Pb in soil and plant tissue as a result of trace element emissions could damage plants and adversely affect the health of animals consuming vegetation in the affected areas. (4) Plants may be damaged by NOx emissions since estimated NOx concentrations approach or exceed threshold concentrations. (5) Sensitive plant species may be damaged by predicted short-term SO2 concentrations which are in the damage threshold range.

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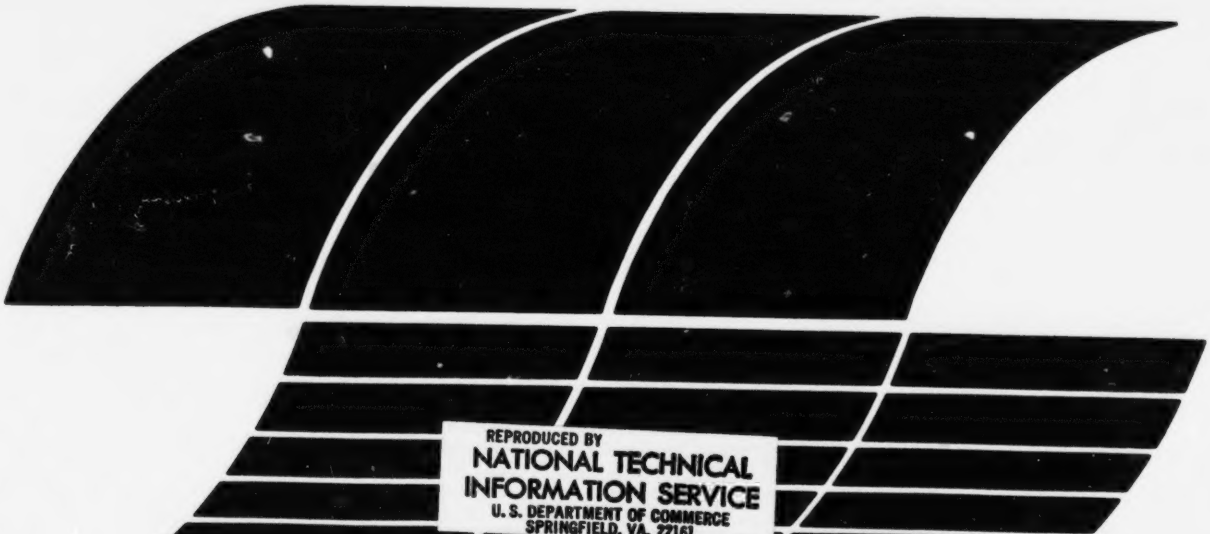

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ABSTRACT

A comprehensive multimedia emissions assessment was performed on the cyclone-fired La Cygne No. 1 boiler. The unit is equipped with SO_2 and particulate emission control. Level 1 and Level 2 procedures were utilized to characterize pollutant emissions in gaseous, liquid, and solid process streams. Results of the comprehensive assessment, in conjunction with assumed typical and worst case meteorological conditions, were utilized to estimate the environmental impact of emissions from this type of unit. Principal conclusions indicated are as follows: 1) The risk of violating National Ambient Air Quality Standard (NAAQS) for 24 hour and annual average levels is low. However, units utilizing high sulfur fuel may exceed short term NAAQS for SO_2. 2) Little adverse health effect is anticipated as a result of SO_2, $SO_4^=$, and particulate emissions projected from widespread use of coal-fired units of the type tested. 3) Increases in the concentrations of cadmium and lead in soil and plant tissue as a result of trace element emissions could cause plant damage and adverse health effects to animals consuming vegetation in the affected areas. 4) Plant damage due to NO_x emissions is likely to occur since estimated NO_x concentrations approach or exceed threshold concentrations. 5) Damage to sensitive plant species may result from predicted short-term SO_2 concentrations which are in the damage threshold range.

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METRIC CONVERSION FACTORS AND PREFIXES

CONVERSION FACTORS

To convert from	To	Multiply by
Degrees Celsius (°C)	Degrees Fahrenheit (°F)	$t(°F) = 1.8\ t(°C) + 32$
Joule (J)	Btu	9.478×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilojoule/kilogram (kJ/kg)	Btu/lb_m	4.299×10^{-1}
Megagram (Mg)	Ton (2000 lb_m)	1.102
Megawatt (MW)	Horsepower (HP)	1.341×10^{3}
Meter (m)	Foot (ft)	3.281
Meter^3 (m^3)	Barrel (bbl)	6.290
Meter^3 (m^3)	Foot^3 (ft^3)	3.531×10^{1}
Meter^3 (m^3)	Gallon (gal)	2.642×10^{2}
Nanogram/joule (ng/J)	lb_m/million Btu	2.326×10^{-3}
Picogram/joule (pg/J)	lb_m/million Btu	2.326×10^{-6}

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
Peta	P	10^{15}	1 Pm = 1×10^{15} meters
Tera	T	10^{12}	1 Tm = 1×10^{12} meters
Giga	G	10^{9}	1 Gm = 1×10^{9} meters
Mega	M	10^{6}	1 Mm = 1×10^{6} meters
Kilo	k	10^{3}	1 km = 1×10^{3} meters
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter
Micro	µ	10^{-6}	1 µm = 1×10^{-6} meter
Nano	n	10^{-9}	1 nm = 1×10^{-9} meter
Pico	p	10^{-12}	1 pm = 1×10^{-12} meter

SECTION 1
INTRODUCTION

Conventional methods for conversion of fuels into usable forms of energy historically have impacted all segments of the environment. Most conventional combustion processes emit sulfur oxides, nitrogen oxides, carbon oxides, particulate matter and other potentially harmful pollutants to the air. Solid wastes from the combustion process, or from control technologies associated with it, present potential disposal problems, as well as health and environmental problems. Adverse water-related health and ecological effects may result when chemical compounds and heavy metals are leached from solid residues.

Conventional fuel combustion processes are playing an increasing role in the movement toward national energy independence. As a result, the potential for adverse environmental impact is also increasing. In recognition of these facts, IERL-RTP established the Conventional Combustion Environmental Assessment program (CCEA) to conduct comprehensive assessments of the effects of combustion pollutants on human health, ecology, and the general environment. The assessments will result in recommendations for control technology and standards development to control adverse effects within acceptable limits.

This report details results of a comprehensive multimedia emissions assessment performed at the La Cygne No. 1 utility boiler in Kansas. This unit is a supercritical cyclone-fired boiler with a net electric generating capacity of 820 MW. High sulfur, high ash, subbituminous coal is typically burned in Unit No. 1. Sulfur and particulate emissions are controlled by limestone scrubbers. Based on 1978 data, cyclone-fired units comprise only 11% of the installed generating capacity from bituminous and subbituminous coal-fired utility boilers. The average installed capacity for cyclone-fired boilers is 250 MW, nearly 3.5 times smaller than the test unit. Further, 61% of all cyclone-fired units (83% on a capacity basis) utilize electrostatic precipitators for particulate control. Hence, emissions from the tested unit should not be considered typical for coal-fired utility boilers. Owing to the high ash and sulfur contents of the La Cygne fuel, the unit's capacity and method of emission control, measured emissions from the La Cygne No. 1 unit may be atypical for cyclones in general. Emissions data presented herein should be considered in light of these limitations and extrapolation should be avoided.

SECTION 2

SUMMARY AND CONCLUSIONS

A comprehensive multimedia emissions assessment was performed on the number 1 unit at the La Cygne power station in Kansas. This unit is operated by Kansas City Power and Light Company (KCP&L) although it is owned jointly by KCP&L and Kansas Gas and Electric Company. The unit is a cyclone-fired Babcock and Wilcox supercritical, once-through boiler with a net electrical output of 820 MW. Typically, a high sulfur, high ash subbituminous coal is burned as fuel. Coal is obtained locally from surface mines owned by KCP&L and operated by Pittsburgh and Midway Coal Mining Company. Emissions of SO_2 and particulates are controlled by eight venturi-absorber scrubber modules utilizing limestone slurry. Spent scrubber slurry is discharged to a 0.65 km^2 settling pond. Water for cooling purposes is drawn from a 10.5 km^2 cooling reservoir constructed adjacent to the plant site.

Major effluent streams from the site are flue gas, combined bottom and fly ash, scrubber solids, settling pond overflow and ash pond overflow. With the exception of the ash pond overflow, samples were obtained from each of these streams. Characteristics of the ash pond overflow were estimated from analyses of liquid discharged into the ash pond from the ash dewatering tanks.

Flue gas emissions are summarized in Table 2-1. Tabulated emissions of NO_x represent lower limit values since samples were collected in bags and sample degradation has since been determined significant. The apparent NO_x removal by scrubbing is attributed to degradation of the bag samples rather than actual removal from the flue gas. No attempt was made to accurately measure CO emissions; indicated upper limits result from a 1000 ppm detection limit.

Measured SO_2 emissions indicate 78% removal by scrubbing which exceeds the design removal efficiency of 76%. Approximately 98% of uncontrolled sulfur emissions were as SO_2 while 1.1% and 0.4% were as SO_3 and particulate $SO_4^=$, respectively.

TABLE 2-1. SUMMARY OF FLUE GAS POLLUTANT EMISSIONS

Pollutant	Emission Factor, ng/J	
	Before Scrubber	After Scrubber
NO_x[*] (as NO_2 near full load)	≥715	≥385
CO[†]	≤520	≤520
SO_2[‡]	3380 ± 400[***]	740 ± 90[***]
SO_3[**]	48 ± 24[***]	10 ± 11[***]
SO_4[**]	22 ± 9.0[***]	2.7 ± 1.9[***]
Total Organics[††]	2.77 - 4.07	1.45 - 2.60
Total Particulates[‡‡]	1090 ± 270[***]	80
Cl^-[**]	<0.1	<0.1
F^-[**]	0.6 ± 0.4[***]	<0.14

[*] NO_x was determined by chemiluminescent analysis of bag samples (Level 2). Due to potential for NO_x degradation in bag samples, measured values are considered to be lower limit values. Apparent NO_x removal by limestone scrubbing is attributed to sample degradation.

[†] CO was determined by gas chromatographic analysis of bag samples (Level 2). Indicated values represent the detection limit of 1000 ppm.

[‡] SO_2 was determined by pulsed fluorescence analysis of bag samples and by the CCS (Level 2).

[**] SO_3, SO_4^-, Cl^-, and F^- were determined by analysis of the CCS (Level 2).

[††] C_1-C_{16} fractions were determined by gas chromatograph while the $>C_{16}$ fraction was determined gravimetrically (Level 1). Upper limit values include detection limits of fractions which were not detected.

[‡‡] Total particulates were determined by a modified Method 5 procedure (Level 2) and from the SASS train particulate catch (Level 1).

[***] Indicated uncertainties represent one standard deviation.

Total particulate emissions data indicate 91% removal by scrubbing which is lower than the design removal of 98%. Scrubber inlet particulates consisted primarily of particles larger than 3 μm; 13% of the particulates were 3-10 μm and 87% were larger than 10 μm. After scrubbing, 82% were less than 1 μm, 11% were 1-3 μm, 1% were 3-10 μm and 6% were larger than 10 μm. Scrubber removal efficiencies were essentially zero for particles smaller than 3 μm and approximately 99% for particles larger than 3 μm.

Atomic absorption analysis (AAS) was utilized to determine concentrations of 18 trace elements in the flue gas. Concentrations of most elements exceeded health-based Discharge Multimedia Environmental Goal (DMEG) values at the scrubber inlet. At the scrubber outlet As, Cd, Cr, Fe, Ni, Pb, and Zn exceeded their respective health-based DMEG values. Comparison of AAS data with spark source mass spectroscopy (SSMS) analysis indicated that SSMS corresponds to the more accurate AAS results only to within one or two orders of magnitude for most elements.

Speciation of organic compounds in the flue gas indicated the presence of aliphatic hydrocarbons, substituted benzenes, ethylbenzaldehyde, dimethylbenzaldehyde, 2,6-pereriden-dione-4, and 2,6-dimethyl-2,5-heptadion-4-one, and the methyl ester of long chain acid, at concentrations ranging from 0.2 to 20 g/m^3 prior to scrubbing. Only ethylbenzaldehyde, substituted benzenes, and aliphatic hydrocarbons were identified at the scrubber outlet. Most POM compounds identified at the scrubber inlet are naphthalene, substituted naphthalenes, biphenyl and substituted biphenyls. Concentrations of these compounds were several orders of magnitude lower than their respective DMEG values. No POM compounds were detected at the scrubber outlet.

Liquid wastes were analyzed by AAS to determine trace elements and by gas chromatograph to determine organics. Liquid to the ash pond was found to contain Al, Ca, Cd, Fe, V, and Zn at concentrations exceeding ecology-based DMEG values while only Fe exceeded its health-based DMEG value. The scrubber slurry settling pond overflow contained Ca, Cd, Mn, Ni, and Pb at concentrations exceeding health and ecological DMEG values and, in addition, Al, Fe, and Zn exceeded their respective ecological DMEG values. Total organics were detected at 0.06 mg/l in liquid to the ash pond and at 0.6 mg/l in settling pond overflow. Liquid to the ash pond did not contain >C_{16} organics while the settling pond overflow organics were primarily >C_{16}.

AAS analysis of solid wastes indicated that Al, As, Ca, Cd, Fe, Mn, Ni, Pb, and Zn concentrations in scrubber solids, and Al, Ca, Cr, Fe, Mn, Ni, Pb, and Zn concentrations in bottom ash/fly ash samples exceeded health-based DMEG values. Organic concentrations in scrubber solids and bottom ash/fly ash samples were 6.6 mg/kg and 86.2 mg/kg, respectively. No organics $>C_{16}$ were detected. POM compounds were not detected in scrubber solids.

Bioassay tests were performed on six samples obtained at the La Cygne unit: 1) cyclone particulate catch (scrubber inlet); 2) raw limestone; 3) combined bottom ash/fly ash; 4) scrubber outlet slurry solids; 5) cooling water; and 6) scrubber outlet slurry. Tests performed include Ames mutagenicity assay, CHO clonal toxicity, RAM cytotoxicity, WI-38 human cell cytotoxicity, rhodent toxicity, and freshwater toxicity assays. In general, no toxicity was detected. However, the RAM cytotoxicity assay indicated low toxicity for bottom ash/fly ash, scrubber outlet solids, and the cyclone particulate catch. Also, the scrubber outlet slurry exhibited low toxicity in WI-38 cytotoxicity assay and moderate toxicity in the CHO cytotoxicity assay.

An environmental impact assessment was performed based upon emission rates measured at the La Cygne number 1 boiler and assumed typical and worst case type meteorological parameters. Principal conclusions indicated by this assessment are as follows:

- The environmental acceptability of emissions from coal-fired boilers is largely dependent on site-specific factors such as background pollution levels and meteorology. However, the risk of violating NAAQS due to criteria pollutant emissions from a coal-fired boiler (874 MW gross output scale) like La Cygne utilizing a cyclone furnace appears low in terms of 24 hour and annual average levels. Units utilizing high sulfur fuel, such as that utilized in the La Cygne number 1 boiler, may exceed short term NAAQS for SO_2.

- Based on the Lundy-Grahn Model for health effects associated with suspended sulfate levels, limited adverse health effects would result from these emissions. Similar results were obtained with this model considering the effects of SO_2 and total particulate emissions on people older than 30 to 40 years of age.

- The impact of trace element burdens on drinking water and air quality as a result of measured emissions from this coal-fired utility boiler is generally orders of magnitude less than allowable or acceptable exposure levels. However, substantial increases in Cd are predicted in soil. Similarly, substantial increases in Cd and Pb are predicted in plant tissues. While long-term accumulation of Cd may cause plant damage and serious health effects to animals consuming vegetation in the affected areas, accumulation of other trace elements is not expected to result in concentrations which would be toxic to human or plant life.

- Plant damage due to NO_x emissions is likely to occur since estimated NO_x concentrations (both short and long term) approach or exceed threshold concentrations. Predicted short term concentrations of SO_2 are also in the threshold range; hence, SO_2 emissions may result in damage to sensitive plant species. Plant damage is not likely to result from predicted concentrations of other criteria pollutants. The effects of secondary pollutants formed by reactions between NO_x and hydrocarbons, and the synergistic effects of SO_2 in the presence of ozone are uncertain.

SECTION 3
TEST SETTING

PLANT DESCRIPTION

The coal-fired utility boiler tested was the number 1 unit at the La Cygne power station in Kansas. The unit is operated by Kansas City Power and Light although it is owned jointly by KCP&L and Kansas Gas and Electric Company. It burns local coal and has an air quality control system for reducing SO_2 and particulate emissions.

The La Cygne Station is located about 88 km south of downtown Kansas City, Missouri, and 0.8 km west of the Missouri state line. The plant site was selected primarily because of availability of coal, water and limestone locally. Figure 3-1 shows general plot plan of the entire facility. Figure 3-2 shows the general material flow diagram for the unit tested.

Boiler

Boiler Number 1 was designed to burn coal as the primary fuel. It is a cyclone-fired, super critical, once-through, balanced draft Babcock & Wilcox unit rated at 46.8 Mg/s of steam. This corresponds to a maximum heat input rate of approximately 137 GJ/s. The generator is rated at 874 MW, gross (measured at the generator with no allowance for powering fans or pumps). The net output, that is the power leaving the plant, is 820 MW. Construction of the unit began in 1969. Commercial operation began in mid-1973.

Figure 3-3 is a schematic of the boiler. Figure 3-4 shows a schematic of the burner-cyclone furnace combination. In most boilers the fuel and all or part of the combustion air are mixed in the burner but the bulk of the actual fuel burning occurs in the boiler (more accurately called the boiler furnace). In cyclone-fired units the fuel-air mixture is ejected from the burner into the cyclone furnace. The cyclone furnace is a barrel shaped plenum into which the combustion air is injected (see Figure 3-4). Essentially complete

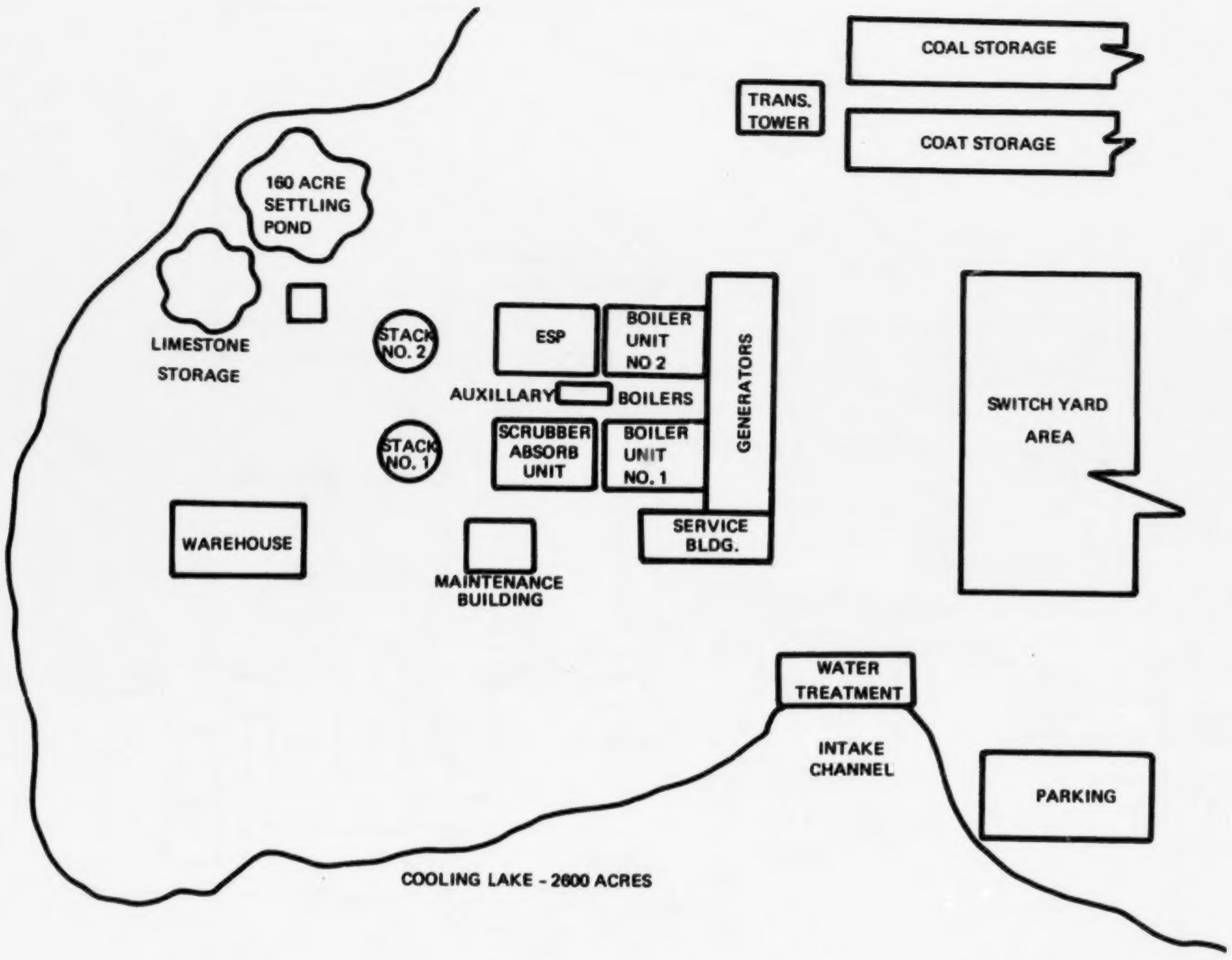

COAL STORAGE
TRANS. TOWER
COAT STORAGE
160 ACRE SETTLING POND
LIMESTONE STORAGE
STACK NO. 2
STACK NO. 1
ESP
BOILER UNIT NO 2
AUXILLARY
BOILERS
SCRUBBER ABSORB UNIT
BOILER UNIT NO. 1
GENERATORS
SERVICE BLDG.
SWITCH YARD AREA
WAREHOUSE
MAINTENANCE BUILDING
WATER TREATMENT
INTAKE CHANNEL
PARKING
COOLING LAKE - 2600 ACRES

Figure 3-1. Layout of Plant Site

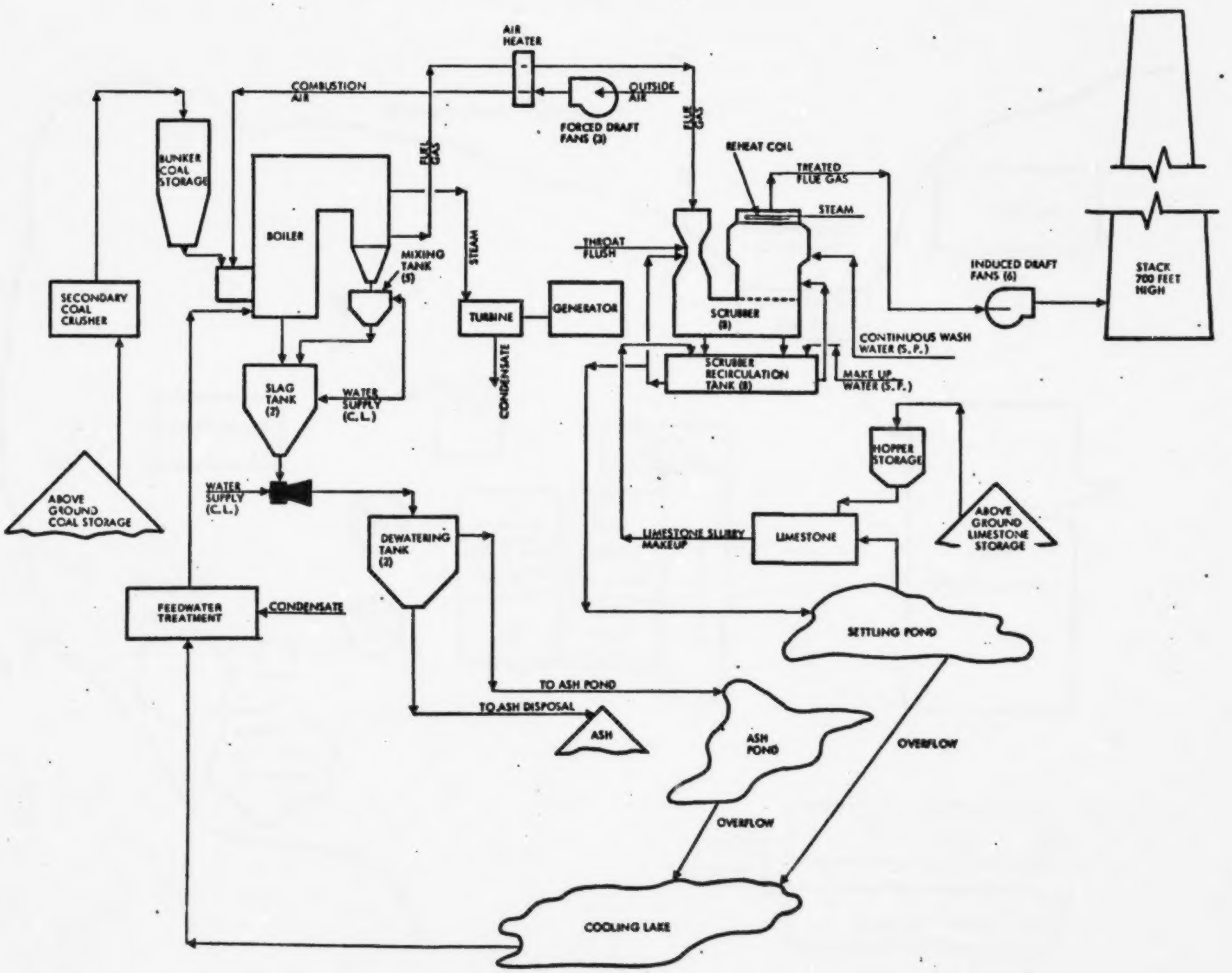

AIR HEATER
COMBUSTION AIR
OUTSIDE AIR
FORCED DRAFT FANS (3)
FLUE GAS
FLUE GAS
REHEAT COIL
TREATED FLUE GAS
STEAM
BUNKER COAL STORAGE
BOILER
MIXING TANK (5)
STEAM
THROAT FLUSH
SCRUBBER (8)
INDUCED DRAFT FANS (6)
STACK 700 FEET HIGH
SECONDARY COAL CRUSHER
TURBINE
GENERATOR
CONTINUOUS WASH WATER (S. P.)
SCRUBBER RECIRCULATION TANK (8)
MAKE UP WATER (S. P.)
SLAG TANK (2)
WATER SUPPLY (C.L.)
CONDENSATE
HOPPER STORAGE
ABOVE GROUND COAL STORAGE
WATER SUPPLY (C.L.)
DEWATERING TANK (2)
LIMESTONE SLURRY MAKEUP
LIMESTONE
ABOVE GROUND LIMESTONE STORAGE
FEEDWATER TREATMENT
CONDENSATE
SETTLING POND
TO ASH POND
TO ASH DISPOSAL
ASH
ASH POND
OVERFLOW
OVERFLOW
COOLING LAKE

Figure 3-2. Material Flow Diagram

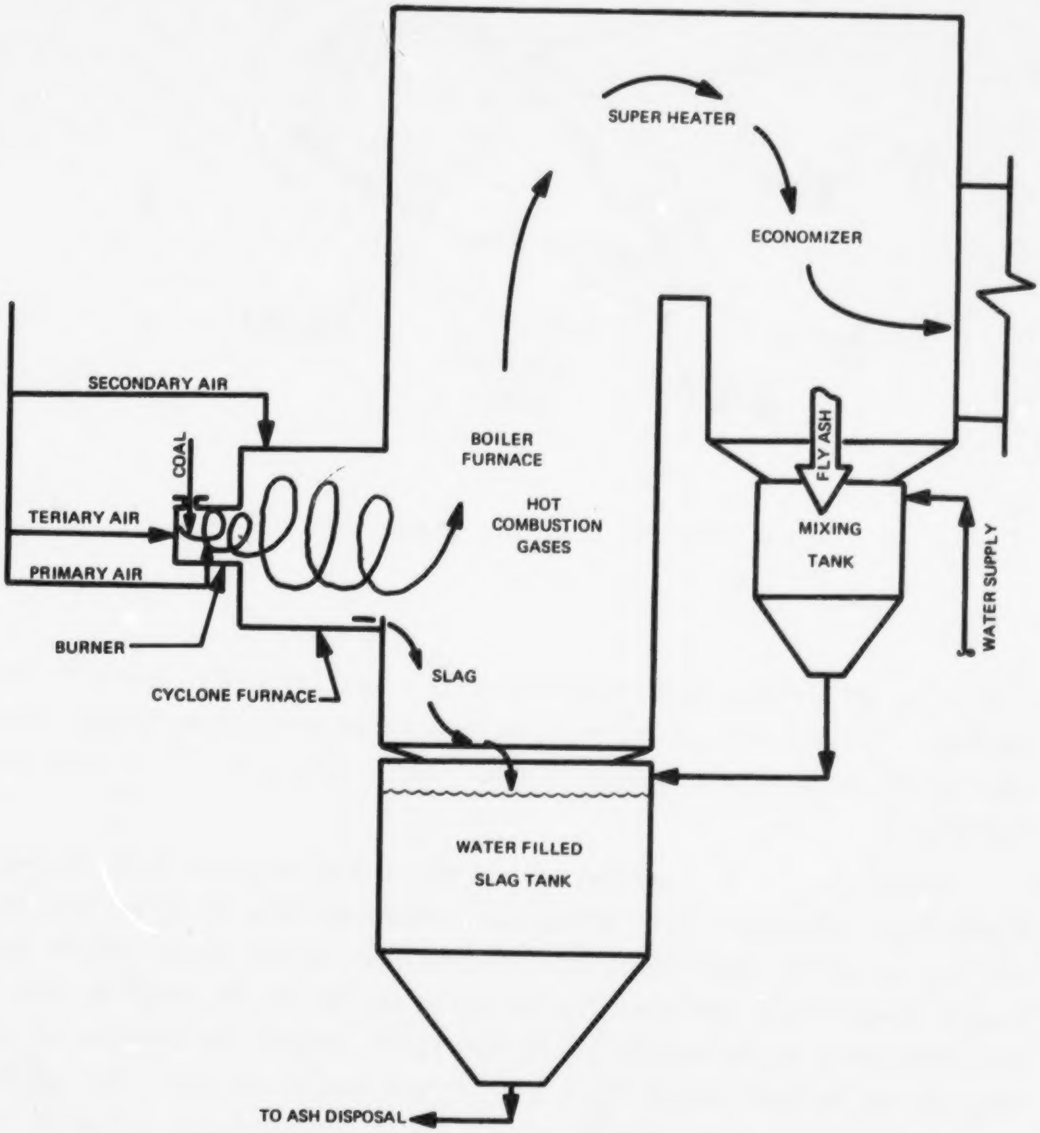

SUPER HEATER
ECONOMIZER
SECONDARY AIR
COAL
BOILER FURNACE
HOT COMBUSTION GASES
FLY ASH
TERIARY AIR
MIXING TANK
PRIMARY AIR
WATER SUPPLY
BURNER
SLAG
CYCLONE FURNACE
WATER FILLED SLAG TANK
TO ASH DISPOSAL

Figure 3-3. Schematic of Boiler

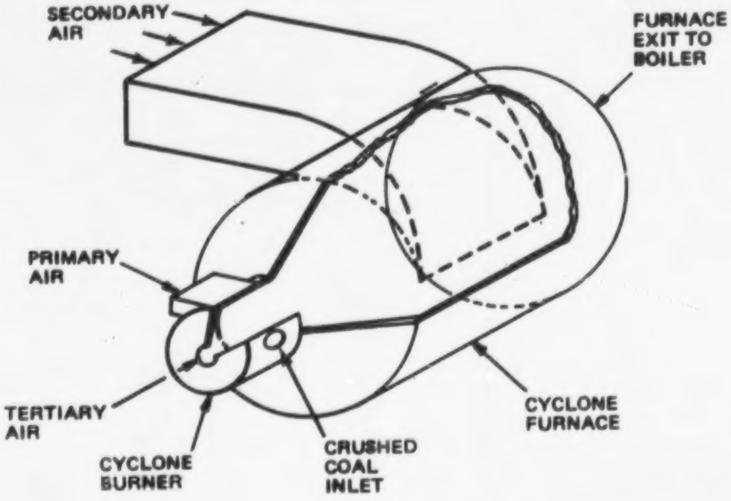

SECONDARY AIR
FURNACE EXIT TO BOILER
PRIMARY AIR
TERTIARY AIR
CYCLONE BURNER
CRUSHED COAL INLET
CYCLONE FURNACE

Figure 3-4. Schematic of Burner and Cyclone

combustion of the fuel but relatively little heat transfer occurs in the cyclone. The hot combustion products then enter the boiler furnace where most of the heat is transferred to the steam. This unit has 18 such cyclone furnaces.

Combustion air is supplied to the main boiler unit by three forced draft fans. Combustion air enters the combustion zone at three locations. Primary air which constitutes approximately 20% of the total, enters the burner tangentially and imparts a swirling motion to the incoming coal. Secondary air, approximately 75% of the total, enters the main barrel of the cyclone furnace tangentially and imparts additional swirl and centrifugal motion to the coal. Entrance velocities for secondary air of 91 m/s are typical. Tertiary air, approximately 5% of the total, enters through the center of the burner.

Crushed coal from overhead bunker storage is admitted at the top of the burner. Upon entering the cyclone the fuel is burned quickly and essentially completely. Temperatures are high enough to melt the ash constituents in the fuel and form a liquid slag. Because of the whirling action in the cyclone, the liquid slag and much of the particulate matter are propelled by centrifugal force to the outside of the cyclone. The slag with captive particulates drains to the bottom of the cyclone and then to the boiler furnace. On entering the boiler furnace the liquid slag begins to cool. Prior to solidification it drains from the boiler furnace bottom via a slag tap to a water filled slag tank where further cooling and solidification takes place.

The boiler furnace absorbs most of the heat contained in the hot gases produced in the cyclone furnace. Additional heat transfer occurs in the super heaters, economizer and air heaters.

The boiler is scheduled to operate on a 24-hour per day, 7 days per week basis. It is scheduled to be off line no less than once each year for various types of maintenance.

The coal burned is mined locally. The mining area, located near the site, is owned by the utility company and operated by the Pittsburgh and Midway Coal Mining Company. The coal is surface mined and delivered to the site by 109 Mg off-the-road trucks. The trucks bottom dump their loads into a 908 Mg capacity receiving hopper; the typical top size of this coal as received is 0.8 m. From the receiving hopper the coal is transported through the plant by a network of conveyors.

The coal is low grade sub-bituminous with an as-fired heating value of 20.9 to 22.6 MJ/kg, an ash content of approximately 25%, and a sulfur content of 5 to 6%. It is estimated that the coal deposits are approximately 63.5 Tg.

Under some circumstances coke is mixed with the coal to increase the energy per unit weight of the fuel burned. At times 10 to 20% of the fuel can be coke. No information as to coke supplier and analysis was available; however, no coke was fired during testing.

There are three oil-fired auxiliary boilers which are only used intermittently to provide heat for the plant when Unit No. 1 is down and for powering a 20 MW turbine-generator to provide electricity for powering ancillary equipment during startup.

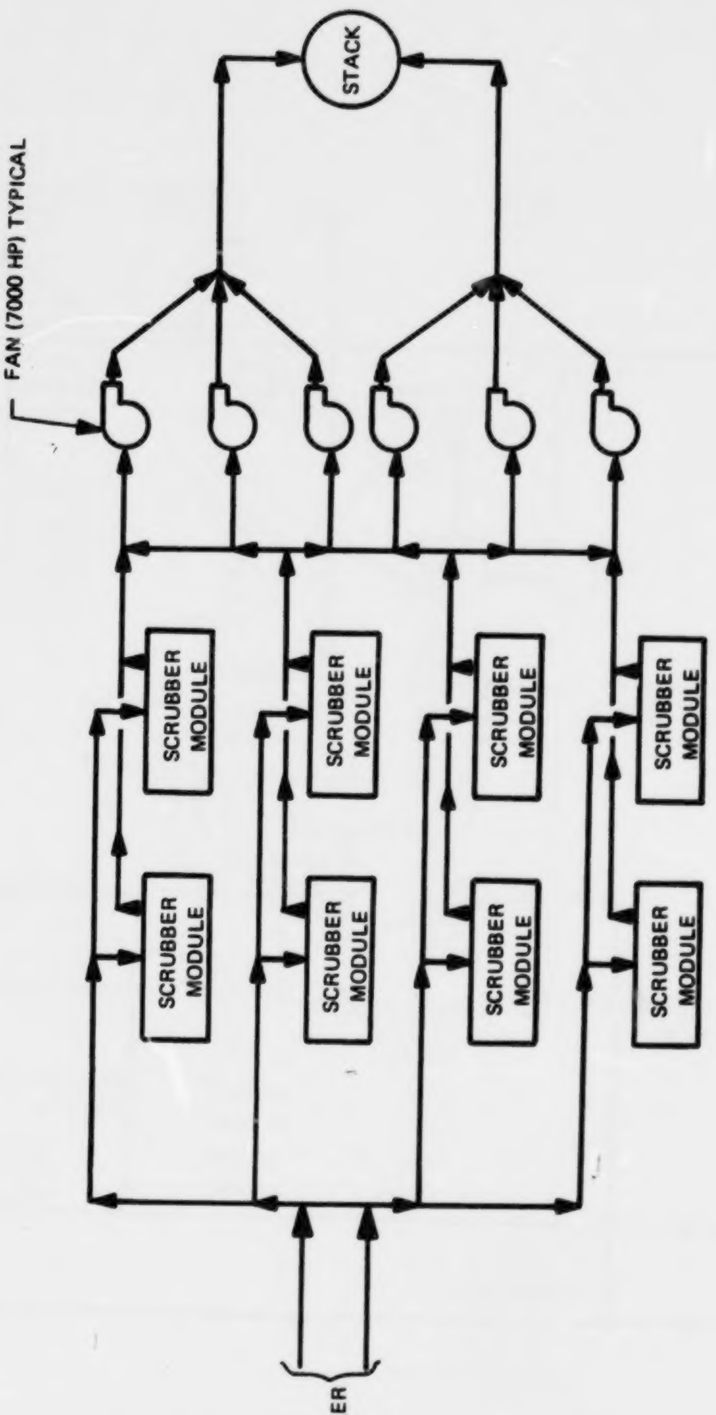
Scrubber

Sulfur dioxide and particulate emissions are controlled by a flue gas scrubber system. The scrubber was designed by Babcock and Wilcox as an integral part of the steam generation plant. It consists of eight two-stage venturi-absorber scrubber modules. The system was designed to treat boiler flue gas at a flow rate of 1209 Nm^3/s. Each module was designed to treat 151 Nm^3/s per module at 413 K.

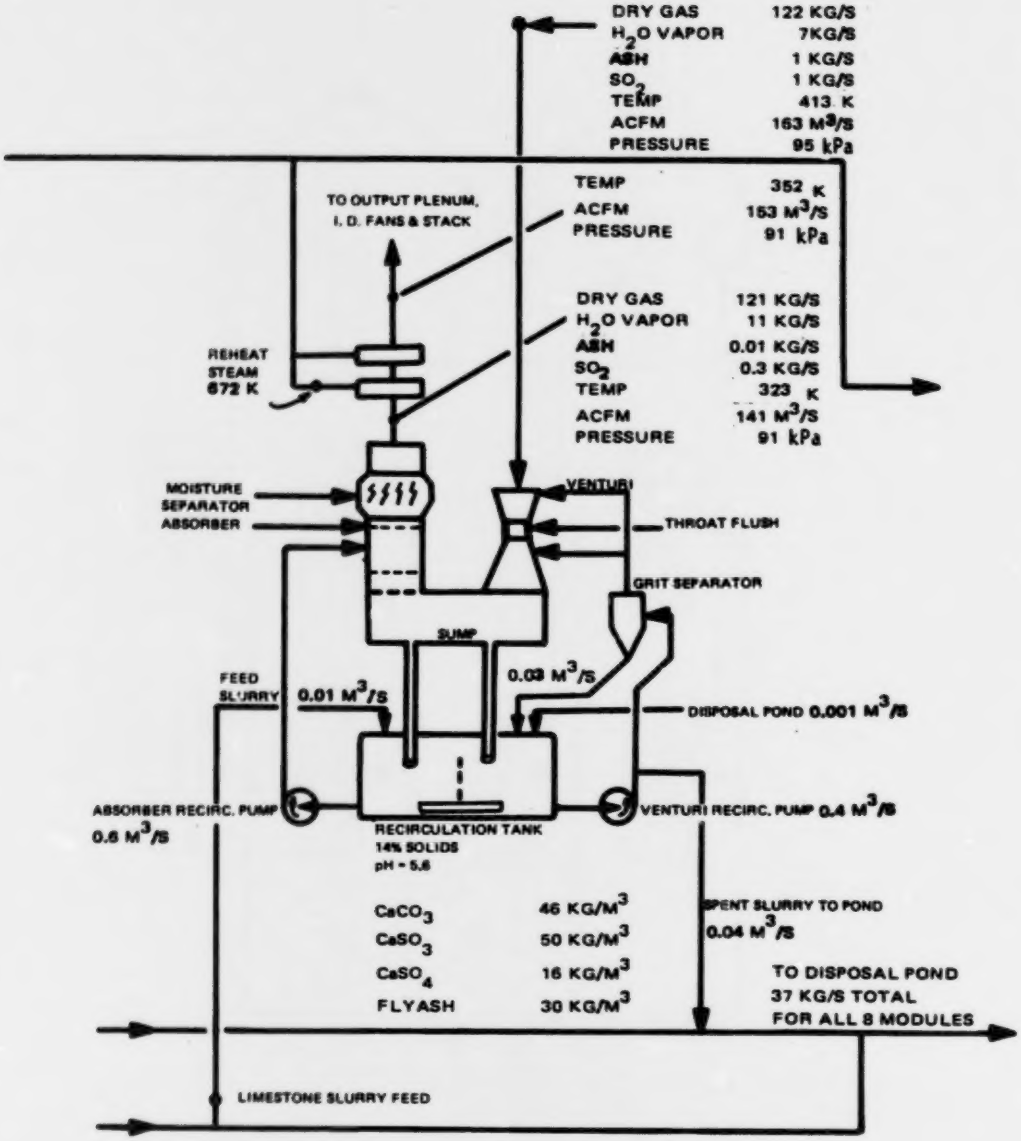
The gas handling system (boiler and scrubber) is balanced draft. Three forced draft fans supply combustion air to the furnace and six fans located downstream of the scrubbing system induce draft in the boiler and scrubber.

As shown in Figure 3-5, the flue gas from the boiler enters the air quality control system through a common plenum. From the common plenum the gas stream is sent to the individual scrubber modules, as indicated. No provisions exist for allowing the flue gas to bypass the scrubber.

As shown in Figure 3-6, upon entering the scrubber module the hot flue gases pass through the venturi section, where they are sprayed with limestone slurry. Up to 99% of the particulate matter is removed from the gas stream at this point. The particles are entrained in the liquid which drops into the bottom sump. The gas stream then makes a 180° turn and passes through the SO_2 absorber section. The SO_2 is removed by absorption as the gas stream is drawn through stainless steel sieve trays which are sprayed with the limestone slurry solution. This slurry with the absorbed SO_2 drops into the bottom sump. The gas stream then passes through a demister section in which excess moisture and mist are removed. The gas stream then passes through a reheat section which increases the gas temperature approximately 303 K to improve gas buoyancy and to reduce the probability of deposits on the induced draft fans. Upon exiting the scrubber module the gas stream enters a common plenum from which it is drawn through one of the six induced draft fans and then sent to the stack. Table 3-1 shows typical characteristics of the flue gas before and after scrubbing, respectively.


FAN (7000 HP) TYPICAL
STACK
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
SCRUBBER MODULE
FLUE GAS FROM BOILER

Figurs 3-5. Scrubber System Flow Diagram


DRY GAS 122 KG/S
H_2O VAPOR 7KG/S
ASH 1 KG/S
SO_2 1 KG/S
TEMP 413 K
ACFM 163 M^3/S
PRESSURE 95 kPa
TEMP 352 K
ACFM 153 M^3/S
PRESSURE 91 kPa
TO OUTPUT PLENUM, I. D. FANS & STACK
DRY GAS 121 KG/S
H_2O VAPOR 11 KG/S
ASH 0.01 KG/S
SO_2 0.3 KG/S
TEMP 323 K
ACFM 141 M^3/S
PRESSURE 91 kPa
REHEAT STEAM 672 K
MOISTURE SEPARATOR
ABSORBER
VENTURI
THROAT FLUSH
GRIT SEPARATOR
SUMP
FEED SLURRY
0.01 M^3/S
0.03 M^3/S
DISPOSAL POND 0.001 M^3/S
ABSORBER RECIRC. PUMP 0.6 M^3/S
VENTURI RECIRC. PUMP 0.4 M^3/S
RECIRCULATION TANK
14% SOLIDS
pH = 5.6
$CaCO_3$ 46 KG/M^3
$CaSO_3$ 50 KG/M^3
$CaSO_4$ 16 KG/M^3
FLYASH 30 KG/M^3
SPENT SLURRY TO POND 0.04 M^3/S
TO DISPOSAL POND
37 KG/S TOTAL
FOR ALL 8 MODULES
LIMESTONE SLURRY FEED

*APPROXIMATE VALUES

Figure 3-6. AQC Module

TABLE 3-1. DESIGN CHARACTERIZATION OF GAS STREAM IN THE AIR QUALITY CONTROL SYSTEM (1 MODULE ONLY)

	Inlet	Outlet
Dry Gas	122 kg/s	121 kg/s
H_2O Vapor	7 kg/s	11 kg/s
Ash	1 kg/s	0.01 kg/s
SO_2	1 kg/s	0.3 kg/s
Temperature	413 K	323 K
Volumetric Flow Rate	163 m^3/s	141 m^3/s
Pressure	95 kPa	91 kPa

The limestone utilized in making up the scrubber slurry is mined locally and brought to the site by off-the-road trucks. Ground limestone is mixed with water for the slurry. The limestone processing and storage facility is capable of supplying 15 Mg/s of slurry to the scrubber system.

The slurry water is recycled from the 6.5 Km^2 settling pond. The flow rate of the makeup water to the system is approximately 0.01 m^3/s.

Sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are removed from the flue gas stream by reaction with the aqueous slurry of limestone. The major component of limestone is calcium carbonate ($CaCO_3$). The products from the SO_2 reaction are carbonic acid (H_2CO_3) and calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2\ H_2O$). The products from the SO_3 reaction are carbonic acid and calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). These reactions are shown below:

$$SO_2 + 1\,1/2\ H_2O + CaCO_3 \rightarrow H_2CO_3 + CaSO_3 \cdot 1/2\ H_2O$$

$$SO_3 + 3\ H_2O + CaCO_3 \rightarrow H_2CO_3 + CaSO_4 \cdot 2\ H_2O$$

The pH of the slurry is maintained at 5.5 to 6.0. Optimum pH for the chemical reactions is 5.6 to 5.8. If the pH exceeds 5.8 the amount of $CaCO_3$ (limestone) required increases and soft scale begins to accumulate rapidly. If the pH drops below 5.6 a hard gypsum ($CaSO_4 \cdot 2\ H_2O$) scale builds up. The pH of the slurry is controlled by adjusting the rate at which limestone is added to the slurry.

Liquid Effluent

The plant produces three major liquid and slurry effluent streams:

- Slurry from the slag tank containing slag and fly ash;
- Spent slurry from the scrubber;
- Effluent from equipment wash down, especially the induced draft fans.

The slurry from the slag tank contains suspended solids from the boiler furnace bottom and the economizer hopper. The solids from the boiler furnace bottom are made up of various non-volatile materials and inorganics which were present in the fuel. The solids from the economizer hopper are made up primarily of fly ash.

Figure 3-7 is a simplified flow diagram of the ash handling system. As shown in the diagram, approximately 0.08 m^3/s is pumped from the cooling water lake into the ash system. Fly ash from the economizer hoppers is gravity fed to the mixing tanks. Fly ash and water are mixed in these tanks and the mixture is piped to one of the slag tanks. Molten slag from the boiler furnace is gravity fed to the liquid filled slag tank. Clinker grinders at the bottom of the slag tank reduce the solidified slag to an appropriate size for transport via jet pumps to dewatering bins. Transport water is drawn from the cooling water lake. Two streams are piped from each dewatering bin. One stream is sent directly to the ash (solid waste) disposal site and the other is piped to the ash pond. Once discharged into the ash pond the suspended solids settle out of the solution and the clear water is recycled to the cooling lake.

The effluent from the scrubbing system is a side stream of the slurry recycling system. Approximately 0.04 m^3/s of spent slurry is discharged from each scrubber module and piped to the on-site settling pond. Table 3-2

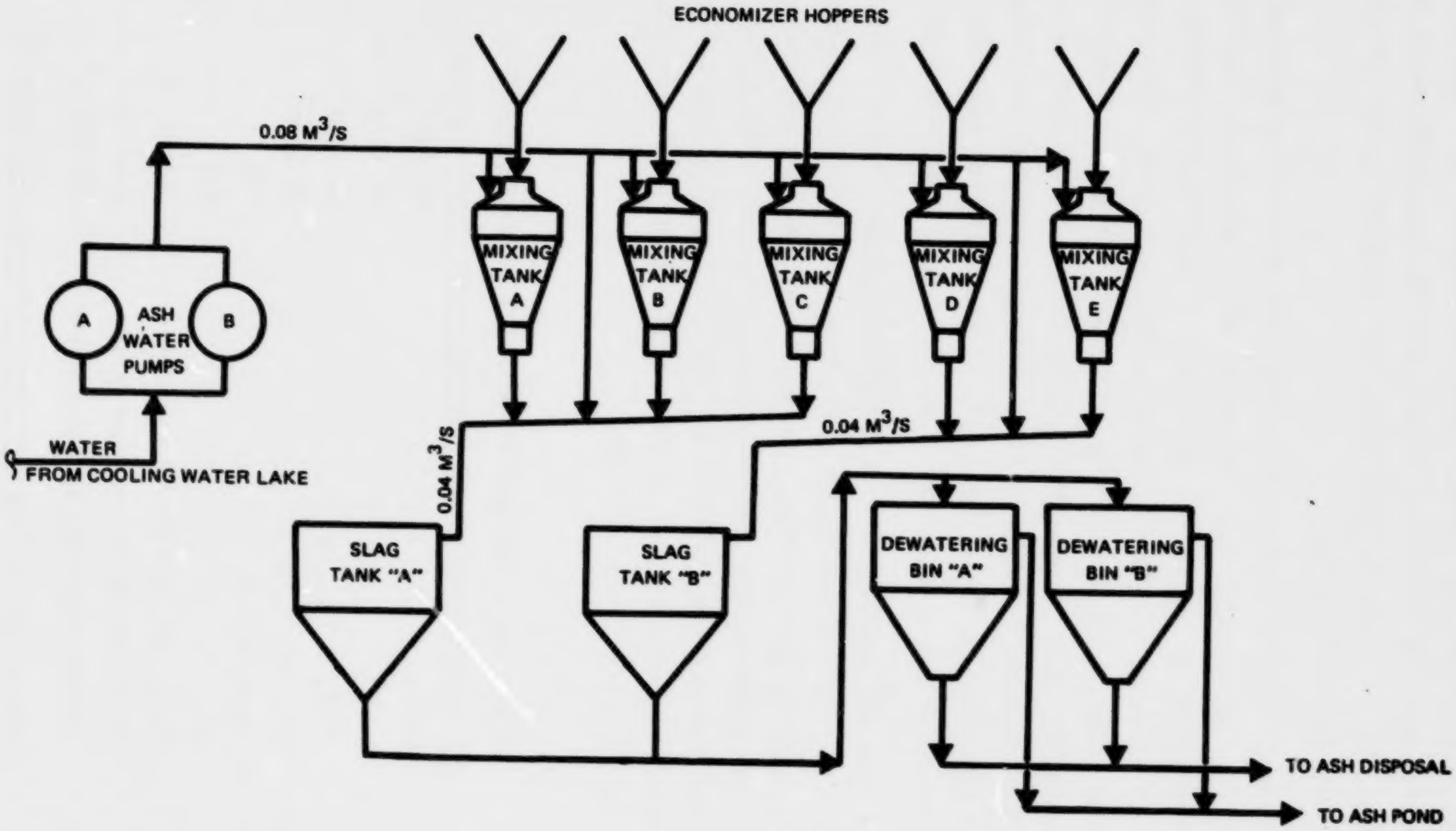

ECONOMIZER HOPPERS
0.08 M³/S
ASH WATER PUMPS
A
B
WATER
FROM COOLING WATER LAKE
MIXING TANK A
MIXING TANK B
MIXING TANK C
MIXING TANK D
MIXING TANK E
0.04 M³/S
0.04 M³/S
SLAG TANK "A"
SLAG TANK "B"
DEWATERING BIN "A"
DEWATERING BIN "B"
TO ASH DISPOSAL
TO ASH POND

Figure 3-7. Flow Diagram Ash Disposal

gives the average analysis of the spent slurry solution. Upon entering the settling pond the slurry is diluted and the suspended solids settle out. The clear solution is recycled to the scrubber system and also discharged into the cooling lake.

Effluents from surface housekeeping wash down and maintenance wash downs (e.g., induce draft fan wash downs) are piped to the settling pond. The settling pond is a 0.65 km^2 pond which is used as the primary sink for the liquid effluent from the air quality control system. Since the pond is an open basin, surface water run-off enters the pond. However, core tests conducted by an independent testing firm indicate that the likelihood of leaching problems is quite remote. Typical water quality parameters for the pond are given in Table 3-3. Part of the clarified water is used as makeup water for the scrubber and part flows to the cooling lake.

The 10.5 km^2 cooling lake is the primary source for all water used by the facility. It receives fresh water from La Cygne Creek, surface water run-off, settling pond overflow, ash pond overflow, and wash down water. Typical lake water quality parameters are presented in Table 3-4. The lake is stocked with various varieties of fish and the plant and KCP&L Company is presently negotiating with several public agencies to open the lake to public use for boating and fishing.

TABLE 3-2. COMPOSITION OF SPENT SCRUBBER SLURRY

$CaCO_3$	46 kg/m^3
$CaSO_3$	50 kg/m^3
$CaSO_4$	16 kg/m^3
Fly Ash	30 kg/m^3
Total Solids	14%
pH	5.6
Total Solids removed per day	3.2 Tg
Total Solids removed per year	0.63 Tg
Volume Displaced by Solids/year	559,000 m^3

TABLE 3-3. SETTLING POND WATER QUALITY

Cations	
Calcium (Ca)	808 ppm
Magnesium (Mg)	106 ppm
Sodium (Na)	53 ppm
Potassium (K)	42 ppm
Anions	
Alkalinity (as HCO_3)	79 ppm
Chloride (Cl)	314 ppm
Sulfate ($SO_4^=$)	1995 ppm
Sulfite ($SO_3^=$)	None detected
Silica (SiO_2)	52 ppm
Others	
pH	8
Conductivity	3500 micromhos/cm
Solids, suspended	5 ppm
Dissolved	3450 ppm

TABLE 3-4. COOLING LAKE WATER QUALITY

Cations	
Calcium (Ca)	126 ppm
Magnesium (Mg)	16 ppm
Sodium (Na)	31 ppm
Potassium (K)	5 ppm
Anions	
Alkalinity (as HCO_3)	112 ppm
Chloride (Cl)	45 ppm
Sulfate ($SO_4^=$)	295 ppm
Sulfite ($SO_3^=$)	None detected
Silica (SiO_2)	1 ppm
Others	
pH	8
Conductivity	820 micromhos/cm
Solids, suspended	5 ppm
Dissolved	610 ppm

Solid Wastes

The solid wastes, primarily ash, generated by combustion are removed from the system as liquid slurries. The solids which settle to the bottom of the settling pond are periodically dredged. The majority of the solid waste is disposed of in a company owned landfill northwest of the facility.

COAL-FIRED UTILITY TESTS

The integrated scrubber, scrubber waste disposal and combustion waste (ash) disposal systems at the coal-fired utility plant are extremely complex. Because the boiler and scrubber were designed and built as an integrated unit a large number of streams had to be sampled to allow a complete characterization of both the boiler and scrubber. A total of 13 separate process streams were sampled. Figure 3-8 shows the sampling location for each stream and Table 3-5 provides stream descriptions. These 13 streams do not constitute all possible sampling locations. However, given the time and budget constraints, these samples did provide sufficient information to conduct a comprehensive emissions assessment of the plant.

Emissions were characterized using EPA's phased approach to sampling and analysis. This approach utilizes two separate levels of sampling and analytical effort (Level 1 and Level 2). Level 1 is a sampling and analysis procedure accurate within a factor of about 3. This level provides preliminary assessment data and identifies problem areas and information gaps. These data are then utilized in the formulation of the Level 2 sampling and analysis effort. Level 2 provides more accurate detailed information that confirms and expands the information gathered in Level 1. The methods and procedures used during this study are, in some instances, modified Level 1 sampling and/or analysis procedures and are documented in the manual, "Combustion Source Assessment Methods and Procedures Manual for Sampling and Analysis", September 1977. The Level 2 methods and procedures included "state-of-the-art" techniques as adapted to the needs of this site. Details of Level 2 procedures are presented in the Appendices. Normally all Level 1 samples are analyzed and evaluated before moving to Level 2. However, because of program time constraints, the Level 1 and Level 2 samples were obtained during the same test period.

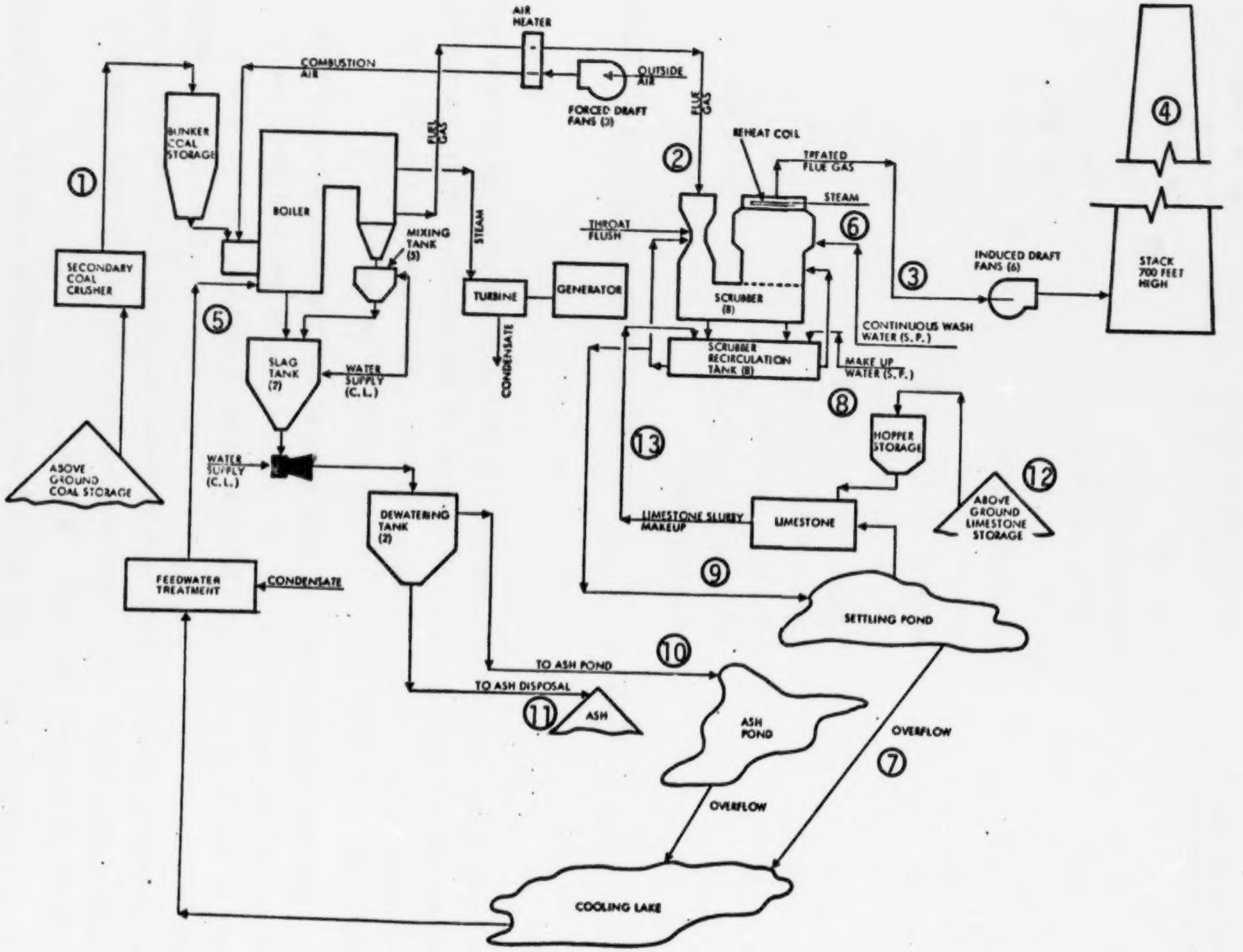

AIR HEATER
COMBUSTION AIR
OUTSIDE AIR
FORCED DRAFT FANS (3)
FLUE GAS
FLUE GAS
BUNKER COAL STORAGE
①
SECONDARY COAL CRUSHER
ABOVE GROUND COAL STORAGE
BOILER
MIXING TANK (5)
STEAM
TURBINE
GENERATOR
CONDENSATE
⑤
SLAG TANK (7)
WATER SUPPLY (C.L.)
WATER SUPPLY (C.L.)
DEWATERING TANK (2)
FEEDWATER TREATMENT
CONDENSATE
②
REHEAT COIL
TREATED FLUE GAS
STEAM
THROAT FLUSH
⑥
SCRUBBER (8)
SCRUBBER RECIRCULATION TANK (8)
CONTINUOUS WASH WATER (S.P.)
MAKE UP WATER (S.P.)
③
INDUCED DRAFT FANS (6)
④
STACK 700 FEET HIGH
⑧
HOPPER STORAGE
⑫
ABOVE GROUND LIMESTONE STORAGE
⑬
LIMESTONE SLURRY MAKEUP
LIMESTONE
⑨
SETTLING POND
⑩
TO ASH POND
TO ASH DISPOSAL
⑪
ASH
ASH POND
OVERFLOW
⑦
OVERFLOW
COOLING LAKE

Figure 3-8. Schematic of Coal-fired Boiler Showing Sampling Locations.

TABLE 3-5. STREAM DESCRIPTIONS

Stream Number	Stream Description	Type of Sample
1	Coal feed	Solid fuel
2	Scrubber inlet	Flue gas
3	Scrubber outlet	Flue gas
4	Stack	Flue gas
5	Boiler feedwater	Liquid
6	Demister wash	Liquid
7	Settling pond overflow	Liquid
8	Scrubber make-up water	Liquid
9	Scrubber feed slurry	Slurry
10	Spent scrubber slurry	Slurry
11	Thickener overflow	Slurry
12	Thickener underflow	Solid ash
13	Limestone feed	Solid

The Source Assessment Sampling System (SASS) was used to collect both gaseous and particulate emission samples at the scrubber inlet and outlet for Level 1 organic and inorganic analysis. The train was run for 6 to 8 hours until a minimum of 30 m^3 of gas had been collected.

Previous sampling and analysis efforts had indicated possible interference of SASS train materials on certain organic and inorganic analysis when at the lower detection limits of Level 2 methods. To avoid this possibility, all glass sampling trains were used to collect Level 2 samples. Two Method 5 sampling trains were modified for Level 2 organic and inorganic sample acquisition. Each train samples approximately 10 cubic meters of flue gas during a 6- to 8-hour run time.

A controlled condensate train (Goksoyr-Ross) was used at each location during testing to obtain samples for SO_2, SO_3 (as H_2SO_4), particulate sulfate, HCl and HF.

During Level 2 test runs, MRI impactors were used to obtain particulate size distribution data for the scrubber outlet gas. However, due to the high particulate loading in the flue gas prior to scrubbing, particulate size distribution data was obtained by polarized light microscopic analysis (PLM) of particulate collected by the modified Method 5 procedure.

Liquid and solid samples were obtained by using appropriate composite dipper and grab sampling techniques.

Each stream was analyzed, as appropriate, for criteria pollutants, inorganics, organics, and wastewater parameters. A variety of analytical techniques were employed to determine both total elemental emissions and, in some cases, specific compounds. These techniques are discussed in detail in the Appendices.

SECTION 4

EMISSION ASSESSMENT OF A COAL-FIRED UTILITY BOILER

TEST CONDITIONS

Five tests were performed on the bituminous coal-fired site. In addition to these five tests, designated 132-136, six runs were made on other days using the Goksoyr-Ross Controlled Condensation System (CCS) to collect supplementary data on SO_2, SO_3, $SO_4^=$, Cl^-, and F^- emissions. These runs are designated I through V and 0, and are discussed in the appropriate sections. Specific conditions for tests 132-136 are summarized in Table 4-1. Unit loading ranged from 620 to 760 MW (gross), which corresponds to between 71 and 87% of full-load operation. Tabulated coal feed rates are nominal, although their accuracies have been estimated from fuel analyses and steam production rates under the assumption of 90% thermal efficiency. Nominal coal feed rates appear to be accurate to within 17%. Because of possible air leakage into the flue gas bag sampling system, two sets of oxygen concentrations were used to calculate emission factors. Oxygen concentrations from gas bag samples were used to calculate SO_2, NO_x, CO, and C_1-C_6 hydrocarbon emissions, since these were also determined from grab bag sampling. Other emissions were calculated using the average oxygen concentration determined by continuous monitoring of the scrubber during runs I-V and 0. Due to possible air leakage into upstream ducting operating at sub-atmospheric pressure, tabulated oxygen concentrations are not necessarily representative of concentrations at the furnace outlet. Oxygen concentrations of 2.8% in the furnace after combustion are typical for this unit during full-load operation; this corresponds to an excess air input of 15% computed using the ultimate coal analysis. During less than full-load operation the excess air level is higher.

Flue gas flow rates were calculated from the oxygen concentration at the scrubber, fuel analyses, and fuel feed rates (estimated from steam production rate data) using the following expression:

TABLE 4-1. SUMMARY OF TEST CONDITIONS

Test No.	Electrical Output (Gross) MW	% of Maximum Load	Nominal Fuel Feed Rate, kg/hr	Steam Production Rate, kg/hr x 10^6	Overall Efficiency* %	Oxygen Concentration		Excess Air At Furnace† %	Flue Gas Flow Rate dscm/s
						Average O_2 at Scrubber %	Average O_2 in Bag Samples %		
132	620	71	254,000	2.27	28	6	7.5	~15	830
133	640	73	254,000	2.34	28	6	9.2	~15	850
134	690	79	295,000	2.38	30	6	8.4	~15	870
135	760	87	318,000	2.77	28	6	8.7	~15	1,000
136	760	87	300,000	2.65	29	6	9.3	~15	970

* Efficiencies are based on the gross electrical output and the steam production rates, assuming 90% efficiency for steam production.

† Values are for full load. For less than full load, slightly higher levels are expected.

$$n_{FG} = \frac{4.762\ (n_C + n_S + .45\ n_N) + .9405\ n_H - 3.762\ n_{O_2}}{1 - 4.762\ (O_2/100)}$$

where:

n_{FG} = gram moles of dry effluent per gram of fuel
n_j = gram moles of element j per gram of fuel
O_2 = volumetric O_2 concentration in percent

Flue gas flow rates are expressed as dry standard cubic meters per second; standard temperature and pressure are defined as 293 K and 101.3 kPa, respectively.

Ultimate analyses of the fuel feed are presented in Table 4-2. Differences among the fuel analyses for the five test days, although generally small, may result from sampling and analysis problems or may reflect actual changes in the feed stock during the test period. However, because of the difficulties associated with sampling large quantities of coal and the limited number of samples acquired, the average coal analysis is considered to be the best estimate of the fuel composition during the test period. Hence, the average analysis was utilized to compute all emission factors presented in this report.

Additional analyses were performed on a coal feed sample from test 135 to determine concentrations of 15 trace elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sr, V, and Zn) and three minor elements (Al, Ca, and Fe). These data are presented in Table 4-3. The coal was analyzed using atomic absorption spectroscopy (AAS), except for aluminum, which was analyzed by neutron activation analysis (NAA).

Considering the uniformity of coal ultimate analyses obtained during the test periods, it appears reasonable to assume that tabulated trace and minor element analyses for test 135 are typical for the coal fired during the five day test period. Although analyses of other coal samples from the same source are not available for direct comparison, analyses of most trace and minor elements presented in Table 4-3 appear to be consistent with concentration limits typifying Appalachian and Eastern Interior Basin coals. No coal strontium analyses were found for comparison. Calcium, lead, and

TABLE 4-2. SUMMARY OF ULTIMATE FUEL ANALYSIS

Component	Test						
	132	133	134	135	136	Average	σ*
Moisture	1.41	1.39	1.30	1.23	1.36	1.34	0.07
Carbon	58.95	56.79	58.13	57.36	55.17	57.28	1.28
Hydrogen	3.93	3.87	3.91	3.79	3.68	3.84	0.09
Nitrogen	0.87	0.93	1.20	1.07	0.98	1.01	0.12
Chlorine	0.03	0.06	0.04	0.05	0.04	0.04	0.01
Sulfur	6.29	5.54	4.57	4.91	5.96	5.45	0.64
Ash	25.19	27.06	26.04	26.24	28.25	26.56	1.03
Oxygen†	3.33	4.36	4.81	5.35	4.56	4.48	0.66
Heating Value (kJ/kg)	24,579	23,800	24,354	23,986	23,502	24,027	384

* σ = one standard deviation.

† Oxygen concentration by difference.

TABLE 4-3. CONCENTRATION OF MAJOR TRACE ELEMENTS IN COAL FEEDSTOCK

Element	ppm in Coal[*]	Typical Range[†] ppm	Reference
Al	2.5%[‡]	0.4-40,700	2, 4
As	36	0.5-93	1, 2
Be	0.1	0.6-4.1	1
Ca	1.2%	0-1,600	2, 4
Cd	24	0.1-65	2
Co	11	0.5-43	1, 2
Cr	41	4-144	1, 3
Cu	3.3	3-61	1, 2
Fe	3.0%	0.3-40,000	2, 4
Hg	1.6	0.07-0.49	1
Mn	114	6-181	2
Ni	45	2-80	1, 2
Pb	2,350[**]	4-218	1, 2
Sb	6	0.2-8.9	2
Se	13	0.4-74	2, 3
Sr	NA	No Data	
V	35[‡]	2-147	1, 2, 3
Zn	1,550	6-5,350	2

[*] Coal sample from test 135. Except where noted, analyzed by atomic absorption spectroscopy.

[†] Typical ranges for Appalachian and Eastern Interior Basin coals.

[‡] Analyzed by neutron activation (Level 2).

[**] The concentration of lead appears inordinately high. However, repeat analyses were not performed.

mercury were found to be present at higher concentrations than are indicated to be typical by the limited published data. Beryllium was found to be at a somewhat lower than typical concentration.

FLUE GAS EMISSIONS

Criteria Pollutants

Federal New Source Performance Standards (NSPS) currently in effect define allowable emission rates of NO_x (as NO_2), SO_2 and total particulates from fossil fuel fired utility boilers having 25 MW or greater output. More stringent limitations have been proposed by EPA for NO_x, SO_2 and total particulate emissions. Federal NSPS currently address neither CO nor total hydrocarbon emissions. Existing NSPS and corresponding proposed emission standards for coal-fired utility boilers are summarized in Table 4-4. It should be noted that this plant is not required to meet NSPS; they are presented for comparison only.

A total of 5 tests were performed to determine the emissions from the coal-fired boiler. A summary of the criteria pollutant emissions data for the 5 test series is presented in Table 4-5. Criteria pollutant emissions data for the individual tests are presented in Table 4-6. Additionally, the average scrubber inlet data are compared with the EPA AP-42 emission factors for uncontrolled sources (5) in Table 4-7. The emissions data are discussed by specific pollutant in the ensuing subsections.

Nitrogen Oxides--

NO_x emissions from the coal-fired boiler were determined by chemiluminescence analysis of grab bag samples. The measured NO_x emission factors near full load conditions were 715 ng/J prior to scrubbing. NO_x data generally indicate a significant reduction of NO_x across the scrubber. However, it has been recently established that NO_x decay inside these grab bags is rapid with respect to time in the presence of air (6). Due to the proximity of the stack sampling location, delays between bag sample acquisition and analysis were at least 30% longer for outlet samples than for inlet samples. Hence, NO_x removal by the FGD system at the coal-fired power plant was probably not a real phenomena but, rather, the result of NO_x degredation in bag samples. Additional data from on-line monitoring would be needed

TABLE 4-4. EXISTING AND PROPOSED FEDERAL EMISSION STANDARDS FOR COAL-FIRED UTILITIES

Pollutant	NSPS	Proposed Standard
NO_x (as NO_2)	300 ng/J (0.7 lb/MM Btu)	260 ng/J (0.60 lb/MM Btu) for bituminous coal; 220 ng/J (0.50 lb/MM Btu) for sub-bituminous coal.
SO_2	520 ng/J (1.2 lb/MM Btu)	520 ng/J (1.2 lb/MM Btu) max. with 85% reduction to 85 ng/J (0.20 lb/MM Btu).
Total Particulates	43 ng/J (0.10 lb/MM Btu)	13 ng/J (0.03 lb/MM Btu) max. with 99% reduction.

TABLE 4-5. AVERAGE MEASURED CRITERIA POLLUTANT EMISSIONS

Pollutant	Emission Factor (ng/J)	
	Before Scrubber	After Scrubber
NO_x* (as NO_2 near full load)	≥715†	≥385†
CO‡	≤520	≤520
SO_2**	3380	740
Total Organics††	2.77-4.07‡‡	1.45-2.60‡‡
Total Particulates***	1090	80

* NO_x was determined by chemiluminescent analysis of bag samples (Level 2).

† Tabulated NO_x emissions are from tests 135 and 136. These two tests were performed at 87% boiler load. Due to possible NO_x degradation in the sampling bags, these values represent lower limit emissions.

‡ CO was determined by gas chromatographic analysis of bag samples (Level 2).

** SO_2 was determined by two Level 2 methods: 1) pulsed fluorescence analysis of bag samples, and 2) wet chemical analysis of the controlled condensation system's impinger catch.

†† The C_1-C_{16} fractions were determined by gas chromatographic analysis while the >C_{16} fraction was determined gravimetrically (Level 1).

‡‡ Upper limit values include detection limits of fractions which were not detected.

*** Total particulates were determined by a modified Method 5 procedure (Level 2) and from the SASS train particulate catch (Level 1).

TABLE 4-6. SUMMARY OF CRITERIA POLLUTANT EMISSIONS

Test No.	Emission Factor (ng/J)							
	NO_x (as NO_2)	CO*	SO_2†	C_1-C_6 Organics	C_7-C_{16} Organics	>C_{16} Organics	Total Organics	Total Particulates
132 Inlet	460	≤500	3210	ND‡	ND‡	ND‡	ND‡	ND‡
132 Outlet	300	≤500	640	ND‡	ND‡	ND‡	ND‡	ND‡
133 Inlet	250	≤500	3440	ND‡	ND‡	ND‡	ND‡	ND‡
133 Outlet	190	≤500	820	ND‡	ND‡	ND‡	ND‡	ND‡
134 Inlet	480	≤500	2970	1-2.3	0.45	1.32	2.77-4.07	1280
134 Outlet	380	≤500	240**	0.85-2.0	0.12	0.48	1.45-2.60	ND‡
135 Inlet	700	≤550	3650	ND‡	ND‡	ND‡	ND‡	900
135 Outlet	370	≤550	ND‡	ND‡	ND‡	ND‡	ND‡	80
136 Inlet	730	≤550	2560	ND‡	ND‡	ND‡	ND‡	ND‡
136 Outlet	400	≤550	770	ND‡	ND‡	ND‡	ND‡	ND‡
Average Inlet	520	≤520	3380††	1-2.3	0.45	1.32	2.77-4.07	1090
Average Outlet	330	≤520	740	0.85-2.0	0.12	0.48	1.45-2.60	80

* CO emission factor was based on the detection limit of 1000 ppm.

† SO_2 emissions were determined from grab bag sampling for test Nos. 132-134, and from the impinger solution of the controlled condensation system for test Nos. 135 and 136.

‡ ND - data not available.

** Determination of SO_2 emissions at the scrubber outlet for test No. 134 appears to be in error. This data point was judged to be an outlier at 90% probability level by the method of Dixon, and discarded in the computation of average SO_2 emissions.

†† Additional data were used to calculate this average; see Table 4-9.

TABLE 4-7. COMPARISON OF CRITERIA POLLUTANT EMISSIONS WITH EPA AP-42 EMISSION FACTORS FOR COAL-FIRED UTILITY BOILERS (CYCLONE)

Pollutant	Emission Factor (ng/J)	
	Test Data Before Scrubber	AP-42 Emission Factor
NO_x (as NO_2 near full load)	≥715	1020
CO*	≤520	18.5
SO_2	3380	4440
Total Organics	2.8-4.1	5.5
Total Particulates	1090	980

*No effort was made to accurately determine CO emissions.

to confirm any NO_x reduction across the scrubber. Although inlet NO_x samples may also be subject to degradation, concentrations determined from these samples may be utilized as lower limit values.

The measured NO_x emissions at both the scrubber inlet and the scrubber outlet exceed the NSPS limit of 300 ng/J for coal-fired utility boilers. The relatively high NO_x emissions are attributed to: (1) higher thermal NO_x generation in cyclone furnaces because of extremely high heat release rates and the resulting high furnace gas temperatures, and (2) high fuel nitrogen content in the coal.

The Environmental Protection Agency is currently developing a low-NO_x coal burner for utility boilers. This burner relies on a distributed fuel/air mixing concept in which fuel and primary air are injected with a moderate axial component. A surrounding secondary air stream is injected with a swirl component for stabilization. Tertiary air for burnout is added axially around the burner periphery. Pilot tests conducted have shown that the EPA burner is capable of reducing NO_x emissions to less than 86 ng/J (7). However, these burners are designed for pulverized coal firing and are not applicable to cyclone furnaces.

Carbon Monoxide--

No effort was made for accurate determination of CO from the coal-fired boiler. The reported CO emission factor of less than 520 ng/J for the coal-fired boiler was based on detection limit of the instrumentation. However, CO emissions should be comparable in magnitude to the AP-42 tabulations.

Sulfur Dioxide--

SO_2 emissions were determined by two methods during the test period. Bag samples of flue gas from the inlet manifold and stack were analyzed for SO_2 by pulsed fluorescence during tests 132 through 134. The controlled condensation system (CCS) was utilized for SO_2 determination during tests 135 and 136.

Average SO_2 emissions were 3380 ng/J prior to scrubbing. These uncontrolled emission factors are lower than the AP-42 value of 4440 ng/J for coal firing. Average SO_2 emission rates from the coal-fired boiler were 740 ng/J after scrubbing. This represents a mean scrubber efficiency of 78% for SO_2 removal. For comparison, the NSPS units for SO_2 emissions after scrubbing are 520 ng/J for coal-fired utility boilers.

The AP-42 value for uncontrolled coal firing is based on approximately 95% of the fuel sulfur being converted to SO_2, whereas the present study found only 75% of the fuel sulfur as SO_2, using the gas bag and the controlled condensation system (CCS) impingers as sampling devices. The remaining sulfur was not accounted for by SO_3 or particulate sulfate and was not detected in other effluent streams. Tests performed recently under the EPA sponsored project "Environmental Assessment of Conventional Combustion Sources" at three lignite-fired utility boilers using the gas bag sampling technique have demonstrated problems with this technique. SO_2 apparently degraded in the gas bag to such an extent that expected SO_2 concentrations of 390, 230 and 670 ng/J were reduced to 96, <1 and <1 ng/J, respectively. These data indicate that the gas bag sampling method is probably not adequate for accurate SO_2 determinations. However, results from bag samples correspond well with SO_2 data from the CCS. This correlation appears to mutually validate these analytical techniques and associated O_2 measurements despite the fact that incomplete sulfur recovery was obtained.

Total Organics--

In the determination of organic emissions, gas chromatographic analyses were performed on grab bag samples of flue gas and catches from the Level 1 sampling (SASS train). Additionally, gravimetric analyses were performed on Level 1 samples to quantify high molecular weight organics. Each bag sample was collected over an interval of 30 to 45 minutes, with a single sample being collected per test. These samples were utilized to measure C_1 to C_6 hydrocarbons. The SASS train collects approximately 30 m^3 of flue gas which are drawn isokinetically during the test. Samples from the SASS train were analyzed to determine organics higher than C_6. The C_7 to C_{16} fraction was determined by gas chromatograph while organics higher than C_{16} were determined gravimetrically.

Average organic emissions were 2.8-4.1 ng/J for coal firing prior to scrubbing. The higher organic value includes the detection limit concentrations for fractions which were not detected and, as such, represents an upper limit. The measured organic emission corresponds well with the AP-42 value of 5.5 ng/J for coal-fired utility boilers.

Emissions of organics after scrubbing were 0.85-2.0 ng/J for the C_1-C_6 fraction, 0.12 ng/J for the C_7-C_{16} fraction, and 0.48 ng/J for the high molecular weight fraction. The data indicate scrubber removal efficiencies of 14% for the C_1-C_6 fraction, 72% for the C_7-C_{16} fraction, and 63% for higher molecular weight fractions.

Total Particulates--

Average emissions of total particulates were 900 ng/J for coal firing prior to scrubbing. The particulate emission factor for the coal-fired boiler tested is in excellent agreement with the AP-42 value of 980 ng/J for coal-fired cyclone boilers. Total particulate emissions after scrubbing were 80 ng/J. This corresponds to 91% particulate removal efficiency for the scrubber. The NSPS limit for utility boilers is 43 ng/J.

Particulate Size Distribution

Size distributions of particulates at the scrubber inlet and outlet were determined by two methods. Due to the high particulate loading at the scrubber inlet, polarized light microscopic analyses (PLM) were utilized to obtain a size distribution in terms of optical diameter and number of particles per size range. All other particulate size distribution determinations involved streams with substantially lower solids loadings and, therefore, a Meteorology Research Institute (MRI) cascade impactor was used. The cascade impactor data differs from PLM analyses in that size distributions are determined in terms of aerodynamic diameter and weight percent in each size range. Thus, data from the two methods cannot be directly compared. For this reason, the PLM data have been converted to the same basis as the impactor data by assuming that particulate density is independent of particle diameter. This is generally a reasonable assumption because the major components of the particulates generated from coal combustion, the aluminosilicates and iron oxides, are known to partition equally among small and large particulates.* With the constant density assumption, the weight distribution in each size range would be proportional to the product of the number distribution and the particulate volume representing the size range. The particulate volume was calculated based on the geometric mean diameter for the size range.

Particulate size distribution data from tests 135 (inlet) and 136 (outlet)† are summarized in Table 4-8. These data show a significant change in particulate size distribution before and after scrubbing. The increase in the fraction of finer particulates across the scrubber indicates that coarse particulates were removed more efficiently than fine particulates. Particulates larger than 3 μm were removed with efficiencies of greater than 99% while particulates smaller than 3 μm actually showed a net increase in emission rates across the scrubber. This net increase raises the possibility that fine particulates may be generated within the scrubber, or that the particulate size distribution may be modified during the high energy scrubbing process. It is more probable that the high particulate loading at the inlet caused agglomeration of the fine particulates on the test train filter. PLM analysis of the resulting sample may not be able to

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*Although data presented subsequently indicate that partitioning of Al may occur, this simplifying assumption was required in order to present all size distribution data in terms of a common basis. The error associated with this assumption is unknown. Raw data from PLM analyses are presented in Appendix C.

†The reason for this choice of runs is discussed in Appendix C.

TABLE 4-8. SCRUBBER INLET AND OUTLET PARTICULATE SIZE DISTRIBUTION *

Aerodynamic Diameter Size Range, Microns	Weight %[†]		Emission Factor (ng/J)		Removal Efficiency, %
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet	
< 1	<0.01	82	<0.1	65.6	<0
1 - 3	<0.3	11	<3	8.8	<0
3 - 10	13	1	117	0.8	99.3
> 10	87	6	783	4.8	99.4
Total	100	100	900	80	91.1

[*] Determined by Level 2 methods.

[†] Size distribution data from test 135 were used for the scrubber inlet while data from test 136 were used for the scrubber outlet. Total particulate loadings from test 135 were used to compute emission factors. The reason for this choice of runs is discussed in Appendix C.

distinguish the agglomerated fine particulates from the larger particulates, and the distribution is probably weighted towards the larger particulates. Since there was no similar problem with the outlet size distribution, removal efficiencies calculated from these data could be less than zero.

In a recent draft document issued by the Health Effects Research Laboratory (HERL) of EPA (8), it is stated that larger particulates (from 3 to 15 µm) deposited in the upper respiratory system (in the nasopharynx and conducting airways) can also be associated with health problems. This is in contrast to the past belief that particulates of health consequence were those less than 3 µm size and deep-lung penetrable. The area of concern now is particulates which are 15 µm and less, which have been designated as "inhalable particulates" (IP). Emissions of inhalable particulates after scrubbing were approximately 75 ng/J.

Sulfur Compounds: SO_2, SO_3, and $SO_4^=$

Sulfur species were determined using several methods. Bag samples of flue gas from the inlet manifold and stack were analyzed for SO_2 using the pulsed fluorescent analyzer during tests 132-134. The CCS was used at the same sampling points during tests 135 and 136 to collect SO_2, SO_3, and $SO_4^=$. Additional testing was performed at the inlet and outlet of one of the eight scrubbers (module "H") using the CCS. These tests are designated I through V (inlet) and 0 (outlet). The above data are listed in Table 4-9. An average of 98.4% of the output sulfur is emitted as SO_2 during uncontrolled coal firing while approximately 1.1% and 0.4% are emitted as SO_3 and particulate sulfate, respectively. Average removal efficiencies were computed by comparing the average inlet and outlet values for each species. The SO_3 and $SO_4^=$ values from test 0 were discarded because of probable entrainment of particulate sulfate at the scrubber outlet sampling point. The outlet SO_2 value for test 134 was also discarded. This low value is thought to be due to sample degradation in the gas bag*. The removal efficiency for SO_2 by the scrubber system averaged 78%, which compares with 76% design removal efficiency (9). About 80% of the SO_3 was also removed by the scrubber.

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*Degradation of SO_2 in gas bags has been suspected in other cases as well, as discussed previously.

TABLE 4-9. SO_2, SO_3, AND $SO_4^=$ EMISSIONS[*]

				Coal Firing			
Sulfur Compound	Test No.	Sampling Points	Sampling Method	Inlet ng/J	Outlet ng/J	Mole % of Total Sulfur Species in Flue Gas	Removal Efficiency, %
SO_2	132	Plenum/Stack	Gas bag	3210	643	--	
	133	"	"	3440	824	--	
	134	"	"	2970	238[†]	--	
	135	Plenum	CCS	3650	ND	97.6	
	136	"	"	2560	ND	97.8	
	I	Module H	"	3260		98.0	
	II	"	"	3450		98.7	
	III	"	"	3980		99.1	
	IV	"	"	3640		98.9	
	V	"	"	3610		98.8	
	0	"	"		766		
	Average			3380	744	98.4	78.1
SO_3	135	Plenum/Stack	CCS	99.4	17.2	2.13	
	136	"	"	53.7	1.87	1.64	
	I	Module H	"	49.3		1.18	
	II	"	"	39.3		0.899	
	III	"	"	23.6		0.470	
	IV	"	"	35.3		0.767	
	V	"	"	38.6		0.846	
	0	"	"		18.8[‡]		
	Average			48.5	9.54	1.13	80.3
$SO_4^=$	135	Plenum/Stack	CCS	15.5	5.09	0.276	
	136	"	"	18.2	2.39	0.464	
	I	Module H	"	41.2		0.826	
	II	"	"	22.2		0.423	
	III	"	"	24.2		0.402	
	IV	"	"	18.6		0.337	
	V	"	"	15.3		0.277	
	0	"	"		15.9[‡]		
	Average			22.2	3.74	0.429	83.1

[*] Level 2 procedures were utilized.

[†] This value was not used in computing averages, as sample degradation in the sample bag was suspected.

[‡] These values were not used in computing averages, as the sampling point was close enough to the scrubber that entrainment of particulate sulfate was probable.

This figure appears to be high as SO_3 is usually associated with water present as fine aerosols in the flue gas stream, which are less efficiently scrubbed. The removal efficiency for $SO_4^=$ averaged 83%, which is lower than the total particulate removal efficiency. This indicates that the $SO_4^=$ may be associated with the fine particulates in the flue gas stream, which are less efficiently scrubbed.

Sulfate emissions broken down into water- and acid-soluble fractions are presented in Table 4-10. This distribution was changed somewhat by scrubbing, as 97% of the inlet sulfates and 99% of the outlet sulfates were water-soluble.

Inorganics

Trace elements present in the flue gas were determined using atomic absorption spectroscopy (AAS). Concentrations of 18 major trace elements present in the flue gas are presented in Table 4-11. To assess the hazard potential of these emissions, the emission concentrations are compared with the Discharge Multimedia Environmental Goal (DMEG) values. The DMEG values are emission level goals developed under direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time (10). The DMEG values tabulated represent air concentrations which were derived from human health considerations based on the most hazardous compound formed by the element in question. Analysis of the flue gas indicates that 16 elements exceeded their respective DMEG values at the scrubber inlet and 7 exceeded their DMEG values at the scrubber outlet. These seven elements which are of potential concern are arsenic, cadmium, chromium, nickel, lead, iron, and zinc. The DMEG value for arsenic is low because it is a cumulative poison producing chronic effects in humans. Considerations for the potential carcinogenic, oncogenic, and teratogenic effects of cadmium upon humans have led to a low DMEG value for this element. Chromium and nickel have low DMEG values due to considerations of potential human carcinogenicity. Lead is a cumulative poison which results in lesions in human organs.

Emission factors for the 18 trace elements analyzed are presented in Table 4-12, as are scrubber removal efficiencies for each element. An overall removal efficiency of 94% was obtained for these trace elements.

TABLE 4-10. SUMMARY OF SULFATE EMISSIONS*

Test No.	Sampling Point	Scrubber Inlet					Scrubber Outlet				
		Water Soluble Sulfates		Acid Soluble Sulfates		Total	Water Soluble Sulfates		Acid Soluble Sulfates		Total
		ng/J	% of Total	ng/J	% of Total	ng/J	ng/J	% of Total	ng/J	% of Total	ng/J
135	Plenum/Stack	>15.5	>99.5	<0.07	<0.5	15.5-15.6	5.09	>98.6	<0.07	<1.4	5.1-5.2
136	"	16.7	91.4	1.6	8.6	18.3	1.3	52.9	1.1	47.1	2.4
I	Module H	>41.2	>99.6	<0.1	<0.4	41.2-41.3					
II	"	>22.2	>99.5	<0.1	<0.5	22.2-22.3					
III	"	23.0	94.9	1.2	5.1	24.2					
IV	"	17.1	92.2	1.4	7.8	18.5					
V	"	>15.3	>99.5	<0.08	<0.5	15.3-15.4					
0	"						15.9	>99.5	<0.07	<0.5	15.9-16.0
Average†		>21.6	96.7	.6	3.0	22.2	7.4	>99.3	<0.07	<0.7	10.5-10.6

* Level 2 procedures were utilized.

† 136 outlet value was not included in the outlet average. This outlying value is attributed to the effects of nonisokinetic sampling.

TABLE 4-11. EMISSION CONCENTRATIONS OF TRACE ELEMENTS - TEST 135[*]

Element	Concentration, mg/m^3		DMEG For Air (Health Basis), mg/m^3	Discharge Severity[†]	
	Scrubber Inlet	Scrubber Outlet		Scrubber Inlet	Scrubber Outlet
Al	130	3.0	5.2	25	0.58
As	0.98	0.94	0.002	500	500
Be	0.021	0.0018	0.002	10	0.9
Ca	49	2.0	16	3.1	0.13
Cd	5.1	0.58	0.010	520	58
Co	0.19	0.013	0.050	3.7	0.26
Cr	1.3	0.12	0.001	1000	100
Cu	1.2	0.19	0.20	6.0	0.95
Fe	400	13	1.0	400	13
Hg	0.095	0.0057	0.050	1.9	0.11
Mn	0.70	0.15	5.0	0.14	0.03
Ni	2.0	0.054	0.015	130	3.6
Pb	11	2.9	0.15	73	19
Sb	0.78	0.27	0.50	1.6	0.54
Se	0.37	0.088	0.20	1.8	0.44
Sr	0.46	0.038	3.0	0.15	0.013
V	0.78	0.083	0.50	1.6	0.17
Zn	100	21	4.0	26	5.2

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[*] Level 2 procedures were utilized.

[†] Discharge severity is defined as the ratio of the discharge concentration to the DMEG value.

TABLE 4-12. EMISSION FACTORS FOR TRACE ELEMENTS - TEST 135*

Element	Emission Factor, ng/J Scrubber Inlet	 Scrubber Outlet	Removal Efficiency, %
Al	49	1.1	98
As	0.37	0.35	4
Be	0.0079	0.00067	91
Ca	18	0.73	96
Cd	1.9	0.21	89
Co	0.069	0.0047	93
Cr	0.48	0.046	90
Cu	0.45	0.072	84
Fe	150	4.9	97
Hg	0.035	0.0021	94
Mn	0.26	0.054	79
Ni	0.73	0.020	97
Pb	4.1	1.1	74
Sb	0.28	0.099	66
Se	0.14	0.033	76
Sr	0.17	0.014	92
V	0.29	0.030	89
Zn	39	7.7	80
Total	265	17	94

---

* Level 2 procedures were utilized.

Because removal efficiencies for Al, Ca, Fe, and Ni are higher than the average trace element removal efficiency of 94%, concentrations of these elements in the particulate appear to be lower at the scrubber outlet than at the scrubber inlet. Similarly, concentrations of non-volatile elements removed with less than average efficiency must be higher in the scrubber outlet particulate than in the scrubber inlet particulate. Highly volatile trace elements such as Hg and Se may not be associated with particulates but may, at least in part, be present as elemental vapors. As such, no conclusion may be drawn regarding particulate concentrations of these elements.

Spark source mass spectrometry (SSMS) analysis results are presented in Table 4-13 for the 17 elements which were also analyzed by AAS (mercury was not analyzed by SSMS). Also presented are ratios of SSMS analyses to AAS analyses. Analysis by SSMS is generally used as a screening tool, and is considered to be less accurate than AAS. Comparison of the 17 elements analyzed by both methods shows good agreement (values within a factor of two) for inlet and outlet concentrations of Co, Ni, Sb, Se, and V. Order of magnitude agreement was obtained for Ca, Cd, Be, Fe, Mn, Pb, Sr, and Zn. SSMS analysis of other elements, such as Al, As, Cu, and Cr, correspond to the AAS values only to within approximately two orders of magnitude.

To characterize the distribution of the major elements present in the flue gas particulates and to look at the depth profile of these elements in the particulates, Electron Spectroscopy for Chemical Analysis (ESCA) and x-ray diffraction (XRD) were performed on particulate samples. ESCA depth profile data are presented in Table 4-14 for selected Method 5 train particulate catches (test 135 inlet and outlet). The data are presented as atom percentages, normalized to 100%, of iron, oxygen, calcium, carbon, silicon, and aluminum. These are relative values, not absolute concentrations, since not all elements present in the particulate are included. However, tentative conclusions may be drawn under the assumption that the elements analyzed constitute the major surface components. The Method 5 filter catches were analyzed on the silicon-containing filter which may have caused some interference.

Data presented in Table 4-14 indicate that the concentration of sulfur in both the scrubber inlet and outlet particulate is enriched at the surface and decreases with increasing depth. A possible mechanism which is consistent

TABLE 4-13. SPARK SOURCE MASS SPECTROMETER ANALYSES OF TRACE ELEMENT EMISSIONS - TEST 135

Element	Concentration, mg/m^3		SSMS[*]/AAS[†]	
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet
Al	1.9	> 0.14	0.015	> 0.05
As	> 95	> 9.0	>97	> 9.6
Be	0.0034	0.001	0.16	0.6
Ca	180	>44	3.7	22
Cd	0.86	0.32	0.17	0.54
Co	0.088	0.007	0.46	0.54
Cr	> 0.97	>26	> 0.75	>220
Cu	> 2.0	>26	> 1.6	>140
Fe	>130	>63	> 0.34	> 4.8
Mn	> 1.6	0.02	> 2.3	0.1
Ni	> 1.0	0.036	> 0.52	0.67
Pb	>100	>90	> 9.1	> 31
Sb	0.89	0.12	1.1	0.43
Se	0.38	0.13	1.0	1.5
Sr	> 1.7	0.047	> 3.6	1.2
V	1.0	0.13	1.3	1.5
Zn	>130	>76	> 1.3	> 3.6

[*] SSMS is a Level 1 analysis.

[†] AAS is a Level 2 analysis for cations.

TABLE 4-14. ESCA DEPTH PROFILE DATA FOR SELECTED SAMPLES FROM THE METHOD 5 SAMPLING TRAIN - TEST 135*

		Scrubber Inlet (Atom Percent)									Scrubber Outlet (Atom Percent)						
Sample	Depth	Fe	O	Ca	C	S	Si	Al	Sample	Depth	Fe	O	Ca	C	S	Si	Al
135-IN-CYC	0	2.5	47.4	1.3	28.0	14.1	4.0	2.7	135-OUT-CYC	0	0	53.6	0.9	20.2	12.5	12.7	<1
135-IN-CYC	100 Å	4.1	38.0	1.7	36.0	8.3	5.8	5.9	135-OUT-CYC	25 Å	0	49.5	1.9	25.1	9.8	13.7	<1
135-IN-CYC	150 Å	4.3	35.0	1.7	38.1	10.2	4.0	6.8	135-OUT-CYC	50 Å	1.9	46.3	1.3	28.1	9.3	13.2	<1
135-IN-CYC	200 Å	4.4	35.3	1.6	38.3	8.7	6.6	5.0	135-OUT-CYC	100 Å	2.1	41.8	1.9	33.7	5.3	15.2	<1
135-IN-CYC	300 Å	5.6	34.9	2.3	40.7	5.3	6.1	5.2	135-OUT-CYC	175 Å	2.8	38.6	2.0	32.2	6.3	12.7	5.3
135-IN-CYC	400 Å	4.8	34.9	2.3	41.2	5.3	6.8	4.7	135-OUT-CYC	275 Å	3.2	36.5	3.1	36.2	4.8	13.6	2.6
135-IN-CYC	500 Å	4.1	35.6	2.5	38.1	5.7	8.1	5.8	135-OUT-CYC	400 Å	3.6	35.7	2.3	35.0	6.1	12.2	5.1
									135-OUT-CYC	500 Å	3.0	33.5	2.9	39.6	4.0	11.5	5.6
135-IN-PFb	0	1.3	51.7	0.7	20.6	16.6	5.8	3.3	135-OUT-PFa	0	0.7	58.1	1.8	9.6	8.5	21.4	<1
135-IN-PFb	50 Å	4.4	60.9	2.4	8.3	11.9	7.6	4.5	135-OUT-PFa	50 Å	1.5	60.6	3.3	3.2	5.8	25.4	<1
135-IN-PFb	100 Å	4.6	60.5	2.7	5.5	9.8	11.9	5.0	135-OUT-PFa	100 Å	2.1	60.6	3.7	3.5	5.2	24.9	<1
135-IN-PFb	150 Å	5.0	60.9	2.4	4.1	8.7	12.5	6.4	135-OUT-PFa	200 Å	2.0	60.5	4.1	1.9	5.2	26.2	<1
135-IN-PFb	200 Å	5.1	60.7	3.0	4.0	8.1	12.4	6.7	135-OUT-PFa	350 Å	2.3	59.9	5.1	2.0	4.3	26.5	<1
135-IN-PFb	300 Å	5.6	58.2	3.2	3.4	7.4	14.3	7.8	135-OUT-PFa	550 Å	3.0	59.9	5.4	1.5	3.8	25.3	4.0
135-IN-PFb	400 Å	5.1	60.4	4.1	<1	7.5	15.4	7.4	135-OUT-PFa	1000 Å	2.9	56.6	6.1	1.9	3.1	24.4	5.0
135-IN-PFb	500 Å	4.0	62.0	3.8	<1	6.9	15.3	8.1									

* Level 2 procedures were utilized.

with this observation involves adsorption or deposition of sulfur-containing compounds on the surface of particulates. Scrubber inlet particulates were found to contain $CaSO_4$ by XRD analysis. Formation is probably by H_2SO_4 adsorbing on and reacting with calcium compounds after combustion, which would result in surface enrichment of sulfur relative to bulk particulate concentrations. The presence of carbon in the bulk of the inlet and outlet cyclone particulate catches indicates unburned coal particles. Bulk concentrations of carbon in the inlet and outlet filter catches appear to be at least an order of magnitude lower than those in the cyclone catches based on data at depths of 200 Å to 1000 Å. This may indicate that unburned coal particulates are mostly found in the larger size fractions. Surface enrichment of carbon relative to bulk concentrations in the filter catches may result from adsorption of organics or, in the case of scrubber outlet particulates, deposition of $CaCO_3$.

Chloride and Fluoride Emissions

Specific anion analysis was performed on extracts from particulate catches and impinger solutions from the Goksoyr-Ross sampling train. Emissions data for chloride and fluoride are presented in Table 4-15. HCl and HF concentrations are measured from the impingers and incorporated in the chloride and fluoride emission factors reported in Table 4-15. Fluorides are removed at greater than 62-84% efficiencies by the scrubber. Computation of chloride removal efficiency is not possible because the chloride concentrations were below the detection limit. Assuming that the chloride level is just below the detection limit, 8% of the fuel chlorine was analyzed in the particulate extract, and the remainder was found in the impinger solution as HCl.

Specific Organic Compounds

Selected samples were analyzed by combined gas chromatography/mass spectrometry (GC/MS) for the identification of organic compounds present. The organic compounds identified include aliphatic hydrocarbons, substituted benzenes, ethylbenzaldehyde, dimethylbenzaldehyde, 2,6-pereriden-dione-4, and 2,6-dimethyl-2,5-heptadion-4-one, and the methyl ester of long chain acid, at concentration levels ranging from 0.2 to 20 $\mu g/m^3$ in the flue gas

TABLE 4-15. CHLORIDE AND FLUORIDE EMISSIONS*

Test	Cl^- Inlet ng/J	Cl^- Outlet ng/J	Cl^- Removal Efficiency %	F^- Inlet ng/J	F^- Outlet ng/J	F^- Removal Efficiency %
135	<0.1	<0.1	--	0.37	<.14	>62
136	<0.1	<0.1	--	0.9	<.14	>84

* Level 2 procedures were utilized.

prior to scrubbing. With the exception of ethylbenzaldehyde, substituted benzenes, and aliphatic hydrocarbons, none of the other organic compounds were identified at the scrubber outlet.

Emissions of polycyclic organic matter (POM) determined by GC/MS are summarized in Table 4-16. Most of the POM compounds identified are naphthalene, substituted naphthalenes, biphenyl, and substituted biphenyls. No POM compounds were identified at the scrubber outlet. POM compounds found at the scrubber inlet are at levels several orders of magnitude below their respective DMEG values.

LIQUID WASTE

The two major wastewater streams are wastewater discharge from the slag tank to the ash pond and overflow from the settling pond for spent scrubber slurry. The flow rates for these two wastewater streams are approximately 2.89 Gg/hr and 0.77 Gg/hr, respectively. Two additional streams were sampled, although these streams are not actually wastewater streams because they are not discharged from the site. These streams are the scrubber make-up water and the scrubber discharge liquid. The scrubber make-up water stream is taken from the settling pond and its analysis should be similar to the settling pond overflow. The scrubber discharge stream is the scrubber slurry liquid and discharges to the settling pond.

TABLE 4-16. POM EMISSIONS FROM COAL FIRING PRIOR TO SCRUBBING - TEST 134[*]

Compound	Emission Concentration μg/m^3	DMEG Value μg/m^3	Discharge Severity
Decahydronaphthalene[†]	0.1	130,000	<0.0001
Ditert-butyl naphthalene[‡]	0.3	230,000	<0.0001
Dimethyl isopropyl naphthalene[‡]	0.3	230,000	<0.0001
Hexamethyl biphenyl[**]	0.6	1,000	0.0006
Hexamethyl, hexahydro indacene	1.0	No data	--
Dihydronaphthalene[†]	0.03	130,000	<0.0001
CIO substituted naphthalene[‡]	0.06	230,000	<0.0001
CIO substituted decahydronaphthalene[†]	1.0	130,000	<0.0001
Methyl naphthalene	1.6	130,000	<0.0001
Anthracene/phenanathrene	0.3	1,590	0.0002
1-1' biphenyl	4.0	1,000	0.004
9,10-dihydronaphthalene[†]/ 1-1' diphenylethene	0.2	130,000	<0.0001
1,1-bis(p-ethyl phenyl)-ethane/ tetramethyl biphenyl[**]	9.0	1,000	0.009
5-methyl-benz-c-acridine[††]	0.2	11,000	<0.0001
2,3 dimethyl decahydronaphthalene[†]	<0.03	130,000	<0.0001
Total	18.7		

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[*] Level 2 procedures were utilized.

[†] The DMEG values for decahydronaphthalene, dihydronaphthalene and any substituted decahydronaphthalene are assumed to be the same as that for tetrahydronaphthalene.

[‡] The DMEG values for alkyl naphthalenes are assumed to be the same as that for methyl naphthalene.

[**] The DMEG value for hexamethyl biphenyl is assumed to be the same as that for biphenyl.

[††] The DMEG value for 5-methyl-benz-c-acridine is assumed to be the same as that for benz(c)acridine.

Water Quality Parameters

Table 4-17 summarizes the waste water parameters for the sampled streams.

Inorganics - Wastewater

Analysis results of major inorganic cations in the wastewater stream from the slag tank to the ash pond and the scrubber slurry settling pond overflow are presented in Table 4-18. Also presented are the analysis results for the scrubber make-up water obtained from the settling pond, and for the scrubber discharge liquid (filtrate from the spent slurry). Of the 18 elements analyzed, iron exceeds its health DMEG value and iron, calcium, aluminum, cadmium, vanadium and zinc exceed their respective ecological DMEG values for the wastewater stream to the ash pond. For the scrubber slurry settling pond overflow, calcium, cadmium, manganese, nickel, and lead exceed both their health and ecological DMEG values, and additionally aluminum, iron, and zinc exceed their respective ecological DMEG values. Comparison of the inorganic data for the scrubber slurry pond overflow and the scrubber make-up water (from the settling pond) indicates that the trace element concentrations for these two streams are almost identical. This agreement supports the reliability and accuracy of sampling and analysis of trace elements for the wastewater streams.

Organics - Wastewater

Concentrations of C_7 to C_{16} organics and high molecular weight ($>C_{16}$) organics measured in the wastewater streams are summarized in Table 4-19. The total organics detected are low, ranging from 0.06 mg for the wastewater to the ash pond to 0.6 mg for the scrubber slurry settling pond overflow.

GC/MS analyses were performed to identify the organic compounds present in the wastewater streams. In the extraction of the aqueous samples, the samples were first acidified to pH 2 and extracted with methylene chloride. The samples were then adjusted to pH 7 and reextracted with methylene chloride. A final extraction was made at pH 11.

The results of the GC/MS analyses are presented in Table 4-20. In general, the detected compounds consist of oxygenates such as ketones,

TABLE 4-17. WATER QUALITY PARAMETERS*

Test No.	pH	Conductivity µmhos/cm	TSS mg/l	Hardness (as $CaCO_3$) mg/l	Alkalinity (as $CaCO_3$) mg/l	Acidity (methyl orange as $CaCO_3$) mg/l	Acidity (phenolphtalein as $CaCO_3$) mg/l	Ammonia Nitrogen mg/l	Cyanide mg/l	Nitrate mg/l	Phosphate mg/l	SO_3^- mg/l	$SO_4^=$ mg/l
SETTLING POND OVERFLOW													
132	6.5	3500	150	2750	--	0	33	1.85	0	0.9	0.30	1750	6000
133	6.5	3600	82	2350	--	0	85	2.5	0	1.3	0.45	0	35
135	7.4	4000	15	2800	74	0	--	--	-	1.7	4.2	0	2250
136	6	4000	0	2800	65	0	--	1.1	0	1.4	0.3	150	2050
WATER TO ASH POND													
132	7.0	850	0	400	--	0	0	0.59	0	0.5	0.22	0	150
133	6.5	870	5	400	--	0	-	0.45	0	0.2	0.25	1.0	4.0
135	7.6	800	15	315	112	0	-	0.32	-	0.7	4.3	0	200
136	6.5	820	5	410	105	0	-	0.68	0	0.7	0.31	5	290

* Level 1 procedures were utilized.

TABLE 4-18. TRACE ELEMENT CONCENTRATIONS IN WASTEWATER DISCHARGES FROM COAL FIRING - TEST 135*

Element	DMEG Value, mg/l		Water to Ash Pond			Settling Pond Overflow			Scrubber Make-up Water			Scrubber Discharge Liquid		
	Health	Ecology	mg/l	Discharge Severity		mg/l	Discharge Severity		mg/l	Discharge Severity		mg/l	Discharge Severity	
				Health	Ecology		Health	Ecology		Health	Ecology		Health	Ecology
Al	80	1.0	3.5	0.044	3.5	1.5	0.019	1.5	1.2	0.015	1.2	0.083	0.0010	0.083
As	0.250	0.050	0.012	0.048	0.24	0.021	0.084	0.42	0.017	0.068	0.34	0.06	0.24	1.2
Be	0.030	0.055	0.0003	0.010	0.005	<0.0008	<0.03	<0.01	0.0001	0.003	0.002	0.0011	0.037	0.020
Ca	240	16	150	0.61	9.1	930	3.9	58	910	3.8	57	380	1.6	24
Cd	0.050	0.001	0.020	0.40	20	0.059	1.2	60	0.052	1.0	50	0.0005	0.01	0.5
Co	0.75	0.25	0.002	0.003	0.008	0.043	0.057	0.17	0.047	0.063	0.19	0.005	0.007	0.02
Cr	0.25	0.25	0.012	0.048	0.048	<0.002	<0.008	<0.008	0.001	0.004	0.004	0.004	0.02	0.02
Cu	5.0	0.050	0.008	0.002	0.2	0.004	0.0008	0.08	0.003	0.0006	0.06	0.004	0.0008	0.08
Fe	1.5	0.25	3.0	2.0	12	1.1	0.73	4.4	0.63	0.42	2.5	0.014	0.0097	0.058
Hg	0.010	0.250	<0.0002	<0.02	<0.0008	<0.00008	<0.008	<0.0003	<0.00008	<0.008	<0.0003	<0.00008	<0.008	<0.0003
Mg	90	86	13.8	0.15	0.16	N/A	--	--	11	1.2	1.2	270	3.0	3.1
Mn	0.25	0.10	<0.38	<1.5	<3.8	1.9	7.6	19	1.7	6.8	17	<0.38	1.5	3.8
Ni	0.23	0.010	0.01	0.04	1	0.70	3.0	70	0.86	3.7	86	0.20	0.87	20
Pb	0.25	0.05	0.030	0.12	0.6	0.60	2.4	10	0.024	0.096	0.5	0.03	0.1	0.6
Sb	7.5	0.20	0.002	0.0003	0.01	0.044	0.0059	0.22	0.041	0.0055	0.21	0.063	0.0084	0.31
Sr	46	No MATE	0.84	0.018	--	6.4	0.14	--	5.9	0.13	--	3.4	0.074	--
V	2.5	0.15	0.25	0.10	1.7	0.064	0.026	0.43	0.080	0.032	0.53	0.095	0.038	0.63
Zn	25	0.10	0.13	0.0052	1.3	2.2	0.088	22	1.7	0.068	17	0.005	0.0002	0.05

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* Determined by Atomic Absorption Spectroscopy (Level 2).

TABLE 4-19. ORGANICS IN WASTEWATER DISCHARGES*

	Concentration, mg/l			
	Water to Ash Pond	Settling Pond Overflow	Scrubber Make-up Water	Scrubber Discharge Liquid
C_7	0	0	0	0
C_8	0.02	0	0	0
C_9	0	0	0	0
C_{10}	0	0	0	0
C_{11}	0.02	0.04	0.04	0
C_{12}	0	0.01	0	0
C_{13}	0	0	0	0
C_{14}	0	0	0	0
C_{15}	<0.01	<0.01	<0.01	0
C_{16}	0.01	0.01	0.01	0
$>C_{16}$	0	0.5	0.3	0.1
Total	0.06	0.6	0.4	0.1

* Level 1 procedures were utilized.

TABLE 4-20. GC/MS ANALYSES OF ORGANICS IN WASTEWATER STREAMS[*]

Compound	Water to Ash Pond			Settling Pond Overflow	Scrubber Make-up Water		Scrubber Discharge Liquid
	Acid Extract[†]	Neutral Extract	Basic Extract	Acid Extract	Neutral Extract	Basic Extract	Basic Extract
Olefin or ketone; C_8 - C_{11}	X						
Tetrachloropropane (possible)	X						
6-chloro-N-ethyl-N'-(1-methyl ethyl)-1,3,5-triazine-2,4-diamine	X						
8-methyl-3a-dihydronaphthalene-one		X				X	
3a,7a-dihydro-5-methyl-indene-1,7(4h)-dione		X			0.3 µg/l	X	
Quinoline		X					
Butyl naphthalene(4) (plus a possible alkyl substituted naphthalene)				4 µg/l			
1-chloro-2,4-hexadiene				0.5 µg/l			
C_6 nitrile or C_5 alcohol						X	
Di-2-ethyl-hexyl ester of nonane dioic acid					2 µg/l		
2,2,5,5-tetramethyl hexane							X
Diphenylheptane (possible)							X

[*] Level 2 procedures were utilized.

[†] Identified compounds are present in this extract at concentrations below 15 µg/l.

alcohols, ethers, and cyclic ethers. Some of these are lightly halogenated. Typical DMEG values for these classes of compounds are greater than 1000 μg. Thus, the levels of organics present in the wastewater streams from coal firing do not appear to warrant any environmental concern.

SOLID WASTE

The two major solid waste streams generated are bottom slag/fly ash from the slag tank and scrubber sludge from the FGD operation. These two solid wastes are generated at the rates of 0.11 Gg/hr and 0.13 Gg/hr, respectively, on a dry basis at full load.

Inorganics

The scrubber sludge is composed predominantly of relatively insoluble solids: 45-60% limestone, 30-45% $CaSO_3 \cdot 1/2\ H_2O$, 5-10% fly ash, 5-10% magnetite, and <2% partially combusted coal on a dry basis[*]. Trace elements in the fly ash may contribute to the leachate from the scrubber sludge and are of special concern. The concentrations of 18 trace and minor elements in the scrubber discharge solids are presented in Table 4-21. With respect to the human health based DMEG values for solids, 9 elements exceeded their DMEG values. Eleven elements exceeded their ecology based DMEG values. This is the consequence of transforming a high volume, low concentration pollution stream to a low volume, high concentration stream which can be more readily contained. The discharge severity for over half of the trace elements analyzed is sufficiently high to warrant disposal of these solid wastes in a specially designed landfill.

The concentrations of 18 trace and minor elements present in the bottom slag/fly ash from coal firing are presented in Table 4-22. In 8 cases, the trace element concentration exceeds its human health based DMEG value for solids, and in 12 cases the ecology based DMEG value is exceeded. Again, specially designed landfills should be considered for disposal of these wastes.

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[*] From PLM analysis.

TABLE 4-21. TRACE ELEMENT CONTENT OF SCRUBBER DISCHARGE SOLIDS - TEST 135*

Element	Concentration mg/kg	DMEG value, mg/kg		Discharge Severity	
		Health	Ecology	Health	Ecology
Al	24,000	16,000	200	1.5	120
As	110	50	10	2.2	11
Be	2.5	6	11	0.4	0.22
Ca	51,000	48,000	3,200	1.1	16
Cd	36	10	0.2	3.6	200
Co	22	150	50	0.15	0.44
Cr	52	50	50	1.0	1.0
Cu	190	1,000	10	0.19	19
Fe	50,000	300	50	170	1,000
Hg	< 1.0	2	50	< 0.5	< 0.02
Mg	0.49	18,000	17,400	0.000027	0.000028
Mn	560	50	20	11	28
Ni	96	45	2	2.1	5
Pb	1,100	50	10	22	110
Sb	38	1,500	40	0.025	0.95
Sr	990	9,200	ND†	0.11	--
V	190	500	30	0.38	6.3
Zn	6,500	500	20	13	320

* Level 2 procedures were utilized.

† ND - data not available.

TABLE 4-22. TRACE ELEMENT CONTENT OF BOTTOM AND FLY ASH - TEST 135[*]

Element	Concentration mg/kg	DMEG value, mg/kg		Discharge Severity	
		Health	Ecology	Health	Ecology
Al	82,000	16,000	200	5.1	410
As	11	50	10	0.21	1.1
Be	8.2	6	11	1	0.75
Ca	66,000	48,000	3,200	1.4	21
Cd	1.2	10	0.2	0.12	6
Co	44	150	50	0.29	0.88
Cr	210	50	50	4.2	4.2
Cu	820	1,000	10	0.82	82
Fe	170,000	300	50	580	3,500
Hg	< 1	2	50	< 0.5	< 0.02
Mg	ND[*]	18,000	17,400	---	---
Mn	700	50	20	14	35
Ni	330	45	2	7.3	200
Pb	160	50	10	3.2	16
Sb	7.0	1,500	40	0.0047	0.17
Sr	280	9,200	ND[†]	0.03	---
V	86	500	30	0.17	2.9
Zn	1,500	500	20	3.0	75

[*] Level 2 procedures were utilized.

[†] ND - data not available.

An overall mass balance for these trace and minor elements is presented in Table 4-23. The percent of the trace element in the influent streams which could be located in the effluent streams is taken as a measure of mass balance closure. Very good mass balance closure was obtained for aluminum, arsenic, and strontium. Closures for most other elements were within a factor of two, but recoveries for beryllium and copper values were >700%, and mercury and lead values were low. Stream flow rates were obtained from several sources and it is possible that uncertainties in several of these which were obtained from design values, contributed to poor mass balance closure for some elements. However, process streams of principal importance to the trace element balance are feed coal, bottom ash, and scrubber slurry solids (inlet and outlet). The generally acceptable trace element balances obtained tend to validate flow rates for these streams. Hence, large closure discrepancies may be the result of analytical problems.

Organics - Solid Waste

Concentrations of C_7 to C_{16} organics and high molecular weight ($>C_{16}$) organics measured in the solid wastes are summarized in Table 4-24. The total organics amount to 86.2 mg/kg for the combined bottom ash/fly ash and 6.6 mg/kg for the scrubber discharge solids. High molecular weight organics were not detected for either solid waste.

Organics present in the bottom ash/fly ash are probably the result of incomplete combustion, or the adsorption of organics by fly ash particulates. Organics are present in the scrubber discharge solids because of the partial removal of these compounds from the flue gas stream in the FGD system. GC/MS analysis of the scrubber discharge solids did not reveal the presence of any POM. Although no other specific organic compound identification information is available, the high trace element content of these solid wastes far outweighs the concern for the organic content. Disposal in specially designed landfills should be satisfactory to handle the potential degree of hazard.

BIOLOGICAL TESTING

Selected process samples including solid, liquid, and slurry samples were submitted for bioassay testing. A listing of the samples tested is as follows:

TABLE 4-23. MASS BALANCE OF TRACE ELEMENTS (FULL LOAD)*

	Influent Streams						Effluent Streams						
Element	Coal Feed kg/hr	Ash Water kg/hr	Slurry Inlet, kg/hr Solids	Slurry Inlet, kg/hr Liquids	Scrubber Water, kg/hr	Total kg/hr	Bottom Ash, kg/hr	Ash Water kg/hr	Scrubber Slurry, kg/hr Solids	Scrubber Slurry, kg/hr Liquids	Flue Gas kg/hr	Total kg/hr	Recovery
Al	11,600	2.1	1,000	3.7	0.40	12,606	9,063	10.5	3,170	0.056	12	12,256	97
As	17	0.11	1.8	7×10^{-4}	0.022	18.9	1.1	0.11	15	0.040	3.9	20.15	106
Be	0.046	0.0013	0.022	3×10^{-4}	2×10^{-4}	0.070	0.91	9.1×10^{-4}	0.33	7×10^{-4}	0.0076	1.25	>1,000
Ca	5,566	1,718	23,772	240	331	31,627	7,291	443	6,737	259	8.2	14,738	47
Cd	11.1	0.11	0.17	0.0015	0.023	11.40	0.10	0.060	4.8	3×10^{-4}	2.4	7.36	65
Co	5.1	0.085	0.071	0.0015	0.016	5.27	4.9	0.0061	2.9	0.0034	0.053	7.86	149
Cr	20	0.0061	3.5	7×10^{-4}	0.0012	23.5	23	0.037	6.9	0.0027	0.52	30.5	130
Cu	1.5	0.015	15	0.0011	0.0029	16.5	91	0.024	25	0.0027	0.81	116.8	707
Fe	13,921	1.8	742	6×10^{-4}	0.35	14,665	19,238	9.1	6,605	0.0098	55	25,907	177
Hg	0.72	2.4×10^{-4}	0.091	2×10^{-4}	5×10^{-5}	0.811	0.11	6.1×10^{-4}	0.13	5×10^{-5}	0.024	0.265	33
Mn	53	3.3	47	0.14	0.64	104	77	1.1	75	0.26	0.61	154	148
Ni	21	0.85	2.2	0.022	0.16	24.2	37	0.030	13	0.13	0.22	50.4	208
Pb	1,091	0.072	1.8	0.0037	0.014	1,093	17	0.91	143	0.020	12	173	16
Sb	2.9	0.072	0.71	0.0018	0.014	3.7	0.77	0.0061	5.0	0.043	1.1	6.9	187
Sr	20	13	135	3.6	2.4	174	31	2.5	131	2.3	0.15	167	96
V	41	0.13	6.4	0.0084	0.023	47.6	9.5	0.76	25	0.064	0.35	35.7	75
Zn	720	3.0	2.85	0.011	0.58	726	167	0.39	857	0.0034	86	1,110	153

[*] Level 2 procedures were utilized.

TABLE 4-24. ORGANICS IN SOLID WASTE STREAMS*

Carbon Number	Concentration, mg/kg	
	Bottom Ash/ Fly Ash	Scrubber Discharge Solids
C_7	0	0
C_8	33.0	0
C_9	28.8	4.7
C_{10}	0	1.9
C_{11}	0	0
C_{12}	0	0
C_{13}	0	0
C_{14}	0	0
C_{15}	0	0
C_{16}	24.4	0
$>C_{16}$	0	0
Total	86.2	6.6

---

* Level 1 procedures were utilized.

- Cyclone particulate catch (test 136 scrubber inlet gas)
- Raw limestone (composite of tests 135 and 136)
- Fly ash/bottom ash (test 133)
- Scrubber outlet slurry solids (composite of tests 135 and 136)
- Cooling water (composite of tests 132, 133, 135, and 136)
- Scrubber outlet slurry (composite of tests 134 and 136)

Detailed test descriptions and analytical results have been reported by Litton Bionetics (11). A summary of the bioassay test results is provided in the ensuing paragraphs.

The six samples were examined for their mutagenic activity as well as for their toxicity effects in the in vitro microbial assays employing Salmonella indicator organisms (Ames mutagenicity assay). The genetic activity of a sample is measured by its ability to revert Salmonella indicator strains from histidine dependence to histidine independence. The toxicity is measured by the reduction in number of colonies growing on n nutrient agar plates. The samples were tested directly and in the presence of liver microsomal enzyme preparations from Aroclor induced rats (referenced as S9).

The samples did not exhibit toxicity with any of the indicator organisms employed directly or in the presence of S9. The tests with all the samples were repeated because of inconsistent population counts with some of the indicator strains in the initial test. The results of the repeat tests indicated that these six samples were not toxic to the indicator strains at any of the doses tested.

The results of mutagenicity assays conducted on these six samples in the presence and absence of metabolic activation systems were negative in the initial as well as in the repeat tests. The repeat tests were conducted with all the samples because of inconsistent population counts observed in the initial test. The tests performed with raw limestone and fly ash/bottom ash were repeated once again with the indicator strain TA1535 in the presence of S9 because of an increase in the number of revertants observed at all doses in the repeat test. The final repeat test performed with this strain using duplicate plates per dose level were negative.

Effects of the two liquid-containing samples, cooling water and scrubber outlet slurry, on the colony-forming ability of cultured Chinese hamster cells (CHO) were determined. Test materials were applied to cell cultures for 24 hours at five concentrations from 10 ml/l to 600 ml/l. The cooling water sample caused only a small depression in the colony-forming ability of the CHO cells. This effect was nearly constant from 30 ml/l to 600 ml/l and did not reduce the relative cloning efficiency below about 85%. Therefore, there was no concentration of cooling water which would reduce the colony number by 50% (EC50), and the cooling water was classified as having nondetectable toxicity.

The limestone scrubber slurry test material was toxic at all applied concentrations. The relative cloning efficiency was 71.6% at the lowest applied concentration of 10 ml/l, and no survivors were obtained at 100 ml/l. Since the EC50 value was determined to be 19 ml/l, the slurry was moderately toxic to CHO cells. It was not established whether the cells responded to the particulate or soluble fractions of the slurry.

Cytotoxic effects of the four solid samples on cultured rabbit alveolar macrophanges (RAM) were determined. Test samples were applied to primary cell cultures for 20 hours at concentrations ranging from 3 mg/l to 1000 mg/l. Five cellular parameters were monitored: percent viability; viability index; total protein; total ATP; and ATP/10^6 cells. Of these five parameters, the ATP content was the most sensitive. Concentrations that reduced the culture ATP content by 50% (EC50) were 250 mg/l for the cyclone particulate catch, 370 mg/l for the scrubber solids, and 1000 mg/l for the fly ash/bottom ash sample. These samples are evaluated to have low toxicity. The raw limestone samples had little effect on the cells and, at the highest dose of 1000 mg/l, all five assay parameters were approximately 90% of the negative control values. As such, the raw limestone had no detectable toxicity.

Rhodent toxicity effects of five samples (the cyclone particulate catch was not tested) were determined by oral administration of sample aliquots at a dose level of 10 g/kg. Test results indicate that the samples are non-toxic when administered to young rats at this dose level. Because neither the male nor female rats died during the 14-day test period, LD50 concentrations for these samples is greater than 10 g/kg.

The cytotoxic effects of the cooling water and scrubber slurry samples on cultured WI-38 human cells were determined. Sample material was applied to cell cultures for 20 hours at concentrations ranging from 3 ml/l to 600 ml/l. Five cellular parameters were examined: percent viability; viability index; total protein; total ATP; and ATP/10^6 cells. The cooling water sample had little effect on the cells at concentrations up to 600 ml/l; the viability index was the most sensitive assay parameter and it decreased at the 600 ml/l dose level to 60% of the negative control. Hence, the cooling water sample was evaluated as having nondetectable toxicity to the WI-38 cells. The limestone scrubber slurry reduced the culture ATP content by 50% at 180 ml/l (EC50 value). The EC50 for the viability index was 350 ml/l and the ATP per 10^6 cells parameter gave about 340 ml/l. Thus, the scrubber slurry sample was evaluated as having low toxicity. The slurry sample produced a strong color reaction with the Lowry reagents and prevented determination of the protein content by this method.

The acute toxicities of raw limestone, fly ash/bottom ash, and scrubber solids were determined for freshwater fish (fathead minnows), invertebrate (Daphnia pulex), and algae (selenastrum capricornutum). Fish toxicity tests were conducted using static acute 96-hour tests, Daphnia tests were conducted using 48-hour static acute tests, and algal assays were bottle tests. In addition, algal assays were also conducted on scrubber slurry and cooling water.

For all samples, no detectable toxicity was observed. For the fish acute assays, LC50 values were greater than 1000 mg/l. For the Daphnia assay with raw limestone, the LC50 was greater than 1800 mg/l and for the other samples LC50 values were greater than 1000 mg/l. Results of the algal assays for the solid and slurry samples indicate that population growth at nominal concentrations of 100, 180, 320, 560, and 1000 mg/l of the test materials was not significantly different from the controls. Assays performed in 100% cooling water indicated 8-15% less growth than lower concentrations or the control. Growth in 10, 32, and 56% cooling water was statistically the same as in the control. Growth in 18% cooling water was 5-15% greater than growth in the control. Algal assays therefore indicated no detectable toxicity.

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SECTION 5
ENVIRONMENTAL IMPACT ASSESSMENT

Future energy policies will affect the social, economic, energy, and physical environments. One of the major policy issues involves intensification of coal utilization. It is essential that the effects of increased coal utilization be determined so that national energy policies may be developed.

This section evaluates the impacts of emissions resulting from coal combustion in utility boilers, based on the La Cygne station test results. As indicated previously, La Cygne is unique with respect to several characteristics including boiler size and furnace type. Hence, environmental impacts estimated from La Cygne data may not be indicative of other coal-fired utility boilers. The analysis is conducted in five parts. The first part introduces background information pertinent to the development of the environmental assessment, including a review of relevant studies, plant emissions, and air quality forecasts. In the succeeding parts, the major health, ecological, and economic impacts resulting from coal firing in controlled utility boilers of the type tested are estimated. The final section assesses the implications of the impacts for energy development by considering: 1) the additional controls which may be needed to mitigate the expected damage levels, and 2) the potential effect of such control needs on energy cost and energy resource development.

INTRODUCTION

Economic and environmental concerns over the nation's energy development policies have precipitated several research efforts to evaluate the consequences of all phases of energy development, from fuel production to fuel end use. To organize the various efforts into a systematic, coordinated, environmental assessment structure, the Environmental Protection Agency is implementing a Conventional Combustion Environmental Assessment (CCEA) Program. This program has been established for the purpose of integrating together separate data generated by past and current studies into a complete environmental assessment of conventional combustion processes. The integration procedure involves coordination and information exchange between EPA related studies to: 1) determine the extent to which the total environmental, economic, and energy impacts of conventional combustion process can be assessed, 2) identify additional information needed for complete assessment, 3) define the requirements for modifications or additional developments of control technology, and 4) define the requirements for modified or new standards to regulate pollutant emissions. The CCEA Program coordinates and integrates current and future studies encompassing a wide spectrum of environmental assessment areas and conventional combustion processes. Integration of these studies, including the present effort, will provide the basis for energy policies which result in the expanded use of conventional combustion processes at reasonable environmental, economic, and energy costs.

AIR QUALITY

Model Plant Emissions

Air quality impacts were estimated based on a hypothetical model plant. The model plant was characterized using emission factors derived from the La Cygne plant test data and assumed meteorological parameters. The model plant was assumed to have the same fuel and boiler characteristics as the La Cygne plant. The criteria pollutant emission rates utilized are shown in Table 5-1. Comparison of the measured trace element emission concentrations with DMEG values revealed that the flue gas contained 7 trace elements which exceeded their DMEG values. Hence, these trace elements were also included in this analysis.

Annual Emissions

Estimated annual emissions for hypothetical coal-fired plants generating 874 MW are presented in Table 5-2. These estimates are based on the emission factors determined for the La Cygne coal-fired plant. The hypothetical plant was assumed to operate at 87% of its maximum load with 29% overall efficiency.

Impact on Air Quality

The duration of exposure is important in determining effects of changing air quality. The highest concentrations occur for short periods (usually less than one hour) under meteorological conditions causing plume trapping.

TABLE 5-1. EMISSION RATES FROM A CONTROLLED 874 MW (GROSS) COAL-FIRED UTILITY BOILER*

Pollutant	Emissions, gm/sec
SO_2	1,940
NO_x	≥1,870
Particulates	200
Organics	3.80 - 6.82
As†	0.92
Cd†	0.55
Cr†	0.12
Fe†	13
Ni†	0.052
Pb†	2.9
Zn†	20

*These emission rates are based upon data from a cyclone-fired boiler burning high sulfur, high ash coal. This unit is not required to meet NSPS and, as such, emission rates may be considered to represent worst case values.

†Trace element concentration in the flue gas exceeded the DMEG value.

TABLE 5-2. ANNUAL EMISSIONS*

	Pollutant	Emission Rate, kg/year	
		Scrubber Inlet	Scrubber Outlet
Gaseous	NO_x	$\geq 4.24 \times 10^{7}$	$\geq 4.24 \times 10^{7}$
	SO_2	2.00×10^{8}	4.39×10^{7}
	SO_3	2.87×10^{6}	5.65×10^{5}
	$SO_4^{=}$	1.32×10^{6}	2.22×10^{5}
	CO	$\leq 3.08 \times 10^{7}$	$\leq 3.08 \times 10^{7}$
	Total Organics	$1.64 \times 10^{5} - 2.41 \times 10^{5}$	$8.59 \times 10^{4} - 1.54 \times 10^{5}$
	C_1-C_6	$5.93 \times 10^{4} - 1.36 \times 10^{5}$	$5.04 \times 10^{4} - 1.19 \times 10^{5}$
	C_7-C_{16}	2.67×10^{4}	7.11×10^{3}
	$>C_{16}$	7.82×10^{4}	2.84×10^{4}
	Total Particulates	6.46×10^{7}	4.7×10^{6}
	$<1\mu$	$< 6 \times 10^{3}$	3.99×10^{6}
	1-3μ	$< 2 \times 10^{5}$	5.2×10^{5}
	3-10μ	6.93×10^{6}	5×10^{4}
	$>10\mu$	4.64×10^{7}	2.8×10^{5}
Liquid	(1) Wastewater: Slag tank to ash pond	1.57×10^{10}	
	(2) Scrubber Slurry: Settling pond overflow	4.21×10^{9}	
Solid	(1) Bottom Slag/Fly Ash	6.01×10^{8}	
	(2) Scrubber Sludge	7.10×10^{8}	

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* Coal-fired plants generating 874 MW (gross) operating 6278 hours/year.

The stack emissions are trapped under an inversion layer, with the plume spreading downward. The frequency of occurrence and the severity of such trapping conditions varies depending on the site. As a conservative worst case estimate in this study, plume trapping conditions were assumed to persist for periods as long as three hours. Typical 24 hour maximum concentrations were estimated assuming Gaussian steady state plume dispersion under conditions of low wind speed and stable atmosphere. Typical 24 hour levels were translated to annual expected concentrations by applying ratios for the one day maximum and annual mean as empirically derived from the Continuous Air Monitoring Project (1, 2, 3, 4). The effective stack height was estimated based on assumed meteorological conditions, and the actual stack height.

Table 5-3 shows the maximum predicted levels for criteria pollutants in the vicinity of the model plant. Estimated ambient concentrations resulting from the controlled coal-fired boiler are in excess of the air quality standards for short term SO_x emissions, while concentrations of other criteria pollutants are in conformance with the air quality standards. Carbon monoxide was not accurately measured during testing and will not be considered in this section. It should be noted, however, that CO emissions typically are insignificant relative to NAAQS. For any of the pollutants, the short term maximum concentrations present the most significant air pollution problem. It should be noted that the short term maximum concentrations generally occur infrequently depending on site meteorology, and are usually of very brief duration (about 1 hour or less). The maximum concentration levels are localized within a distance of about one-half to four miles from the boiler stack. These concentrations diminish to about one-half the peak level another one to eight miles further downwind.

The absolute value of the predicted concentrations depends on many variables, not the least of which are assumptions of adverse case meteorological conditions employed in the theoretical air quality models. Stack height is also an important factor which may vary greatly among units, and will generally depend on prevailing meteorology at the boiler site. Meteorological parameters were selected conservatively in the present analysis, resulting in predicted air quality which may be overstated in terms of

TABLE 5-3. COMPARISON OF FEDERAL AIR QUALITY STANDARDS WITH AIR QUALITY PREDICTED TO RESULT FROM COAL COMBUSTION IN A 874 MW UTILITY BOILER

Pollutant	Concentration, µg/m^3				
	Model Plant	NAAQS	PSD Increments**		
			Class I	Class II	Class III
Annual Average*					
NO_x	12	100	---	---	---
SO_2	12	80	2	20	40
Total Organics	0.05	---	---	---	---
Total Particulates	1	75	5	19	37
24 Hour†					
NO_x	46	---	---	---	---
SO_2	48	365	5	91	182
Total Organics	0.2	---	---	---	---
Total Particulates	5	260	10	37	75
1-3 Hour‡					
NO_x	2800	---	---	---	---
SO_2	2900	1300	25	512	700
Total Organics	10	160	---	---	---
Total Particulates	310	---	---	---	---

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* The expected annual average levels were estimated based on the conservative end of the range of typical ratios for 24 hour maximum to annual as reported in the Air Quality Criteria Documents (1, 2, 3, 4).

† Based on typical meteorological conditions for 24 hour period.

‡ Based on worst case meteorological conditions (plume trapping).

** Prevention of significant deterioration standards (PSD).

adversity. However, the calculated levels of air pollutants do illustrate the potentially high concentrations which may occur in the vicinity of some controlled coal-fired utility boilers, and this underscores the necessity for careful siting and design of utilities to avoid potential violations of the NAAQS. Concentrations of total organics are seen to be negligible relative to short term NAAQS. Hence, these emissions will not be considered further.

Federal standards limiting deterioration of air quality are generally more restrictive than the NAAQS. Included in Table 5-3 is a list of the allowable increments of deterioration for the three classes of growth and development areas. Hence, depending on the existing air quality and the allowable deterioration increment, emissions of total particulates from the model plant may not be acceptable in certain locations. Again, siting of the plants would be a major consideration in their environmental acceptability, since areas which already experience marginally acceptable air quality could not tolerate the increases projected to occur.

HEALTH IMPACT

The health effects of exposure to high concentrations of the various pollutants are well known and have been tabulated throughout the literature (5). However, the specific extent to which health is affected by ambient pollutant exposure levels (dose-response relationships) is unclear. Moreover, it is unclear how pollutant specific dose response curves may be related to the overall health effects of the gas-aerosol complex associated with fossil fuel combustion products.

Most attempts to establish dose response functions for ambient pollution levels involve the formulation of some indicator which is then assumed to represent the entire spectrum of primary and secondary pollutants present. The indicator (usually sulfur dioxide, total particulates, or sulfates) is then related to mortality or morbidity data for various areas by various statistical approaches designed to factor out effects of other variables (e.g., population age, climatology, etc.). Dose-response curves derived from these studies are then employed to estimate health effects of air quality changes resulting from proposed projects.

Recently, the health effects model by Lundy and Grahn (6) has been developed for application in the National Coal Utilization Assessment Studies being conducted at Argonne National Laboratories. The model combines mortality functions for suspended sulfates as developed by Finch and Morris (7) and age-dependent and established response curves for cigarette smoke. The mortality dose-response functions for suspended sulfates are based on statistical studies of various populations experiencing different sulfate exposures. Unlike the dose-response air pollution studies, investigations of smokers have been relatively well controlled with respect to age, degree of exposure, and effect. Thus, to expand the predictability of the sulfate dose-response curves to populations of different age distribution (e.g., future populations), the cigarette response curves are adjusted to fit the observed mortality/sulfate data, resulting in a model which predicts age-specific death rates. This elaboration is important because death rates vary exponentially with age, and shifts in the age distribution of a population will result in substantial shifts in total mortality. Accordingly, the Lundy-Grahn Model utilizes projections of the population age distribution to estimate the age-specific and total death rates due to air pollution at any specific time in the future. The basic relationship of the model is:

$$B(X, Xo) = \frac{ae^{bX}}{1 + c\ e^{-d(X-Xo)}}\ S$$

where B is the number of excess deaths per year for the population of age X which was exposed to the sulfate concentration S (in $\mu g/m^3$) since age Xo. The constants a,b,c and d are coefficients to fit the model to cigarette smoking mortality data and response data for a specific population subgroup exposed to air pollution.

The Lundy-Grahn Model is being used in the ongoing National Coal Utilization Assessment Program to estimate excess mortality resulting from increased coal utilization. Air diffusion modeling was conducted first to predict a population-weighted exposure increase for suspended sulfates. The Lagrangian Statistical Trajectory Model of Argonne National Laboratory (8) which assumes a constant transformation of SO_2 to sulfate, is employed in the estimation procedure. Then, based on the predicted exposure increase and projections of the population age distribution, excess death rates are calculated for each age and summed to yield the expected mortality associated with coal combustion. Table 5-4 shows the estimated effects of an average exposure increment of 8.95 $\mu g/m^3$ suspended sulfates predicted to result from coal-firing of power plants throughout the Central United States. The plants are assumed to emit sulfur oxides at the ceiling levels of the NSPS, and the degree of power plant coal firing is assumed to increase in the region from the current level of 161 Tg/y to 744 Tg/y in 2020. The projected levels of power plant coal utilization are predicted to cause significant health effects in future years.

TABLE 5-4. EFFECTS OF COAL COMBUSTION IN POWER PLANTS IN CENTRAL U.S.*

Year	Increase in Death Rate, Number of deaths/ Million persons/Year	Reduction In Expectation of Life At Birth†
1985	28-130	17 - 79 days
2000	181-809	136 days - 1.7 years
2020	150-665	160 days - 1.8 years

* Reference 30.

† The range of values represents the expected and upper 80% confidence limit given by Finch and Morris (7). The effects are calculated corresponding to an expected average exposure increment of 8.95 $\mu g/m^3$ suspended sulfates.

Figure 5-1 shows the expected health effects caused by air pollution (as indexed by suspended sulfates) which might result from coal-fired utility boilers emitting SO_2 at the rate observed in this study, and also the effects which would be expected under coal-firing conforming to the ceiling levels of the NSPS. The maximum impact is expected to occur in the year 2000, when the proportion of population in the highest risk age groups will be greatest. For each million persons, the number of increased deaths expected to occur annually due to accelerated use of coal-fired utility boilers is 222 in the year 2000.

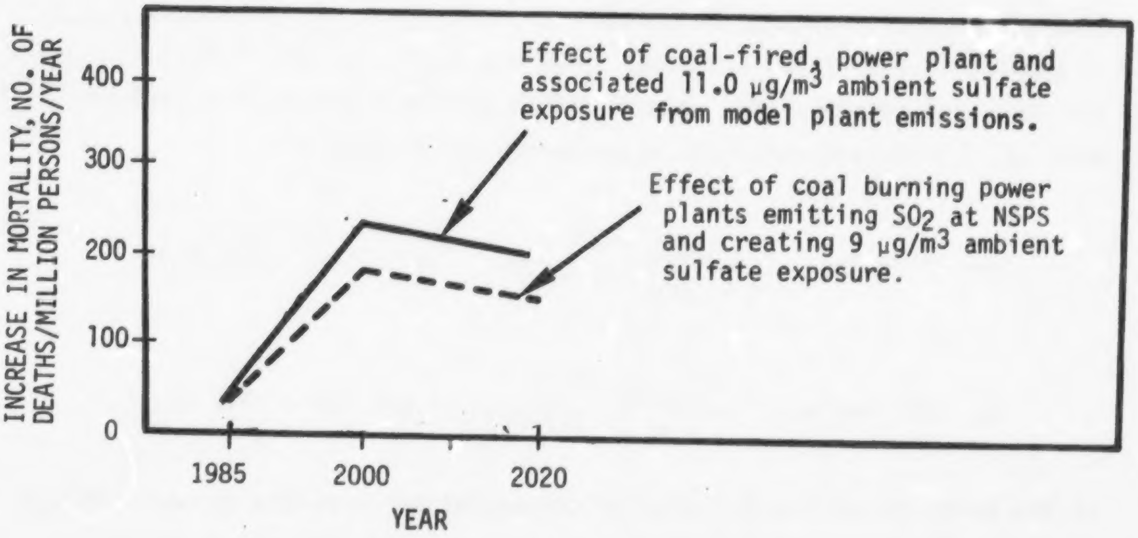

Figure 5-1. Health effects from sulfate levels resulting from coal combustion in controlled utility boilers.

Health effects caused by sulfate levels may also be expressed in terms of morbidity. Table 5-5 presents data for increases in incidents of health disorders due to ambient sulfate exposures. In those areas which already experience high sulfate levels, respiratory disease may increase significantly with increases of suspended sulfates due to increased fuel consumption. For example, in areas where the threshold level 10 $\mu g/m^3$ is exceeded regularly, the contribution of 11.0 $\mu g/m^3$ of sulfate concentration associated with controlled coal-fired boilers would be estimated to produce a 150% increase in the incidence of chronic respiratory disease caused at the threshold level. Based on the expected ambient exposure attributable to coal firing of power plants, other mortality effects (aggravation of asthma, living disease, etc.) would also occur.

In addition to potential health effects created by long range sulfate levels from utility boilers, high concentrations of pollutants in the proximity of the power plant pose a potentially serious health problem. The Lundy-Grahn model may also be applied to estimate mortality effects caused by ambient levels of SO_2 and total suspended particulates. The model gives the following relationships when fitted to Lave and Seskin dose response data (5) for SO_2 and total suspended particulates (TSP):

$$\text{per } 10^6 \text{ males: } \quad \frac{.823e^{.064X}}{1 + 100e^{-.2(X-Xo)}} \quad (.835\ TSP + .715\ SO_2)$$

$$\text{per } 10^6 \text{ females: } \quad \frac{.056e^{.088X}}{1 + 100e^{-.2(X-Xo)}} \quad (.835\ TSP + .715\ SO_2)$$

If the model is applied for average concentrations expected to occur in the vicinity of a power plant (Table 5-3), the expected increase in mortality is appreciable. Figure 5-2 illustrates the estimated impact on mortality. For example, when boilers are coal-fired, populations of the age 50 are predicted to experience increases in death rates of 176 male and 29 female deaths per million persons per year.

TABLE 5-5. HEALTH IMPACTS OF SULFATE AEROSOL*

Pollutant and Health Effect	Population at Risk	Assumed Baseline Frequency of Disorder within Population at Risk	Pollutant Concentration Threshold For Effect	Effect Increase as % of Baseline Per Pollutant Unit Above Threshold
Sulfates				
Mortality	Total Population	Daily death rate of 2.58 per 100,000	25 μg/m³ for one day or more	2.5% per 10 μg/m³
Aggravation of Heart and Lung Disease in Elderly	Same as above for oxidants function	Same	9 μg/m³ for one day or more	14.1% per 10 μg/m³
Aggravation of Asthma	Same as above for oxidants function	Same	6 μg/m³ for one day or more	33.5% per 10 μg/m³
Lower Respiratory Disease in Children	Same as above for nitrogen dioxide function	Same	13 μg/m³ for several years	76.9% per 10 μg/m³
Chronic Respiratory Disease				
Nonsmokers	62 percent of population age 21 or older	Two percent prevalence	10 μg/m³ for several years	134% per 10 μg/m³
Smokers	38 percent of population age 21 or older	Ten percent prevalence	15 μg/m³ for several years	73.8% per 10 μg/m³

* Reference 9.

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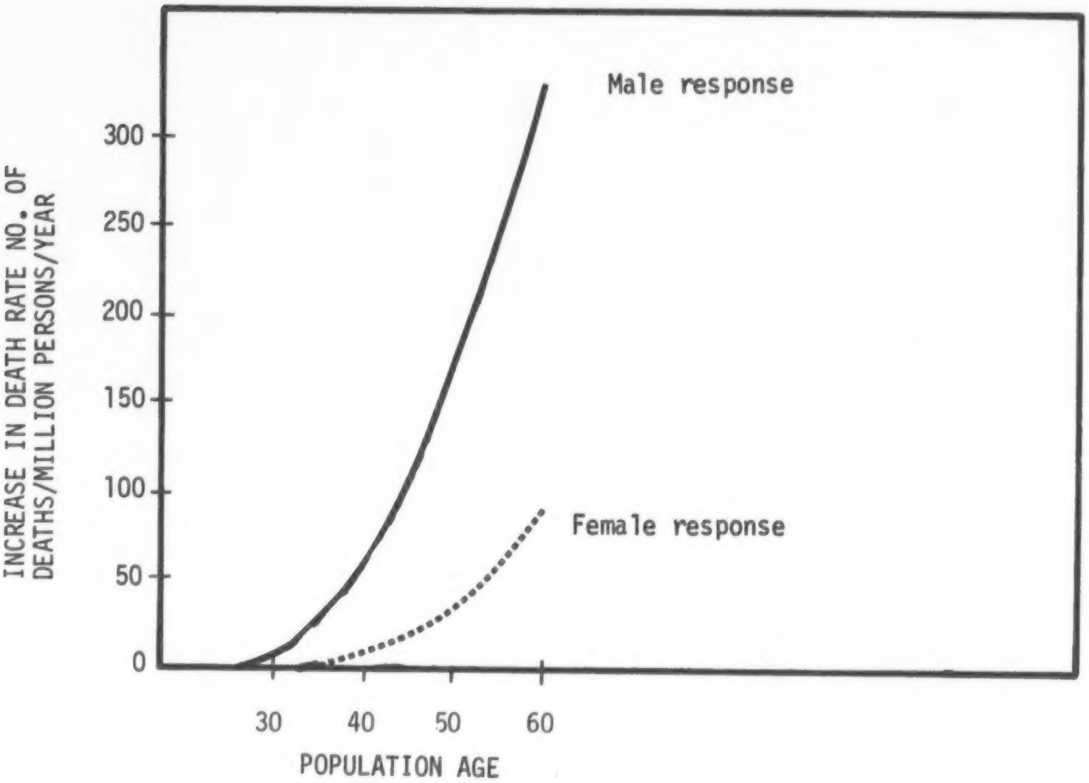

Figure 5-2. Increase in mortality rates in vicinity of coal-fired utility boilers as a result of SO_2 and total particulate emissions.

Effect of Trace Elements--

Trace elements from coal combustion emissions enter the atmosphere and are then dispersed to the upper atmosphere or deposited in the environment around the sources. The principal routes of entry to man are by inhalation, drinking water and food.

Table 5-6 summarizes estimates of the annual average atmospheric concentrations of various elements expected in the vicinity of a single controlled coal-fired utility boiler of 874 MW capacity. The elements included in this listing are those which exhibited stack concentrations

TABLE 5-6. EXPECTED TRACE ELEMENT CONCENTRATIONS IN VICINITY OF A 874 MW CONTROLLED COAL-FIRED UTILITY BOILER

Element	Annual Ambient Concentration, μg/m^3	Typical Urban Air Concentration * μg/m^3	Allowable Exposure Level† μg/m^3
As	0.006	.010	50
Cd	0.003	.300	20
Cr	0.001	.010	50
Fe	0.08	1.60	1000
Ni	0.0003	1.40	100
Pb	0.02	2.40	20
Zn	0.1	.67	500

[*] Based on data reported in References 10, 11 and 12.

[†] Based on ambient air objectives proposed for hazardous waste management facilities (13).

exceeding the DMEG values. Also included in Table 5-6 is a listing of concentrations considered acceptable for continuous ambient exposure. The allowable concentrations are based on proposed regulations for control of air pollution from hazardous waste management facilities, as required by Section 3004 of the Resource Conservation and Recovery Act. It is clear that the air concentrations of elements resulting from operation of the utility boiler are several orders of magnitude (3 to 6) below the allowable exposure level. Moreover, the predicted maximum concentrations are also less than typical urban ambient background levels.

A primary concern in emissions of trace elements is the contribution of these elements to body burden due to exposure to water and food. To estimate this contribution, pollutant deposition rates are approximated by the product of the ambient concentrations and the deposition velocity of the pollutant. The deposition rate is dependent on particle size. Test results of the present study show that particles emitted from the controlled coal-fired boiler are predominantly three μm or less in diameter. The deposition velocity of particles this size over grass surfaces is approximately 0.1 to 0.2 cm/sec (14). Accordingly, the deposition rates of the various trace elements were approximated and are shown in Table 5-7.

The significance of the deposition rates is evaluated by considering the associated effect on drinking water and diet. The pathway to drinking water is by run-off of soil particles containing deposits of trace elements, and the pathway to the diet is by plant uptake from trace elements in the soil. In either pathway, the incremental concentration of elements in the soil determines the extent of the potential impact. Table 5-8 summarizes the maximum predicted soil concentration in the vicinity of coal-fired utility boiler of 874 MW capacity. The concentrations are estimated by assuming mixing of the deposited elements to a depth of 10 cm, and over a period of 40 years. For the majority of the trace elements, only minor increases over the background soil levels would be expected. However, the concentration of cadmium may increase significantly. It is predicted that coal firing will cause an 80% increase in the cadmium soil concentration. The significance of elevated soil concentrations is evaluated by considering the associated increase in trace element concentration in plant tissues and drinking water.

The concentration of elements in plant tissues is related to the biologically available fraction of the elements in the soil. This is often expressed as the soluble concentration in the soil, and is some fraction of the total concentration reported in Table 5-8. Plant possess the ability to concentrate elements from dilute soil solutions. This ability is dependent on the concentration of elements in the soil, and usually increases with decreasing soil concentrations. The ratio of concentration of elements in plants to the concentration in the soil is known as the concentration ratio. Table 5-9 lists average plant concentration ratios for various elements. The data are based on various published data as compiled in a study by Battelle (15). The effect of increased trace element soil loadings (caused by 40 years of boiler emissions) on concentration of the elements in plants is then estimated by assuming that the soluble portion of the loadings are available for plant takeup. For all elements except chromium

TABLE 5-7. ANNUAL DEPOSITION OF TRACE ELEMENTS IN VICINITY OF CONTROLLED COAL-FIRED UTILITY BOILERS

Element	Annual Deposition Rate,* g/m^2-yr
As	3.8×10^{-4}
Cd	1.9×10^{-4}
Cr	6.3×10^{-5}
Ni	1.9×10^{-5}
Pb	1.1×10^{-3}
Zn	7.8×10^{-3}

* Calculated by assuming a particulate deposition velocity of 0.2 cm/sec. The deposition velocity is multiplied by the annual average concentration to estimate the total deposition rate. The deposition rate is calculated for the location where the maximum average annual concentration occurs.

TABLE 5-8. LONG TERM EFFECT OF CONTROLLED COAL-FIRED UTILITY BOILER EMISSIONS ON SOIL CONCENTRATIONS OF TRACE ELEMENTS

Element	Increased Soil Concentration After 40 Years,* mg/kg	Typical Soil Concentration† mg/kg	Increase Over Average Soil Concentrations, %
As	0.1	6.0	2
Cd	0.05	0.06	80
Cr	0.02	40	0.05
Ni	0.01	40	0.02
Pb	0.3	10	3
Zn	2	50	4

* Based on deposition rate (Table 5-7), an assumed mixing depth of 10 cm and soil density of 1.5 Mg/m^3.

† Based on data compiled in Reference 13.

TABLE 5-9. LONG TERM EFFECT OF CONTROLLED COAL-FIRED BOILER EMISSIONS ON CONCENTRATIONS OF ELEMENTS IN PLANTS

Element	Concentration Ratios*	Solubility Of Elements* %	Typical Concentration in plants,* mg/kg	Increase in Concentration of plants,† mg/kg
As	4.2	9	.08- .55	0.04
Cd	222	40	.04- .50	4
Cr	250	0.004	.23	0.0002
Ni	331	0.1	3	0.003
Pb	2	---	2.7	0.6
Zn	40	8	100	7

* Extracted from Reference 15. 3.

Calculated by multiplying concentration ratio by the incremental increase in soil concentration (Table 5-8) by the fraction of the element which is soluble.

and nickel, coal firing appears to exert an appreciable impact on trace element plant burden. The elements predicted to produce the most notable burdens in plant tissue are cadmium and lead. Coal firing is predicted to result in plant concentrations of cadmium about 8 to 100 times greater than the endogenous levels, and is expected to produce a 20% increase in lead concentrations.

Cadmium is considered highly toxic to plants and animals. Mammals tend to absorb cadmium continually, accumulating high body levels which adversely affect the respiratory, cardiovascular, nervous, and reproductive systems, disrupt kidney and liver functions, and cause intestinal disorders. Cadmium levels as low as 15 mg/kg in plants may cause injury to man (16). Cadmium levels in some areas are believed to be approaching threshold levels, and it is believed that cadmium concentrations in cigarettes might cause smokers to exceed thresholds of observable symptoms of cadmium poisoning if exposed to additional sources of cadmium (17). Consequently, the addition of cadmium to the environment in significant quantities is a serious concern.

In contrast to cadmium, lead is considered to exhibit a lower order of toxicity. Both natural and agricultural vegetative species have been found growing in soil with lead concentrations exceeding 700 mg/kg. Soil concentrations of 1000 mg/kg are suspected to be lethal to lettuce. Domestic animals tend to exhibit considerable susceptibility to lead concentration in some situations. It is believed that lead concentrations of 300 mg/kg in foliage will induce lead poisoning in grazing animals. By contrast, animal populations in the wild have been observed in areas with high background levels of lead in soil and vegetation (200-400 mg/kg in the soil and 121 mg/kg in leaves) with no adverse health effects reported.

The actual impact of trace element emissions on plant burden depends greatly on many site-specific variables, such as temperature, precipitation, soil type, water chemistry, and plant species at a given site. Of major concern are the concentrations of elements in soil, water, and the atmosphere. Where trace element concentrations are approaching threshold limits, emissions from power plants will exert a greater influence on health impacts. This consideration is particularly relevant with respect to environmental buildup of cadmium because high background levels of this element already exist in many areas. It is anticipated that long term accumulation of cadmium emissions from coal firing would cause serious health effects to animals consuming vegetation grown in the affected areas. Accumulation of other trace elements in nearby soils is not expected to result in soil concentrations which would be toxic to plants or in plant concentrations toxic to man.

Trace elements also enter the plant via foliar absorption. Intake from the leaf surface to the interior occurs through stomatal openings, walls of epidemal cells, and leaf hairs. Although relatively little is known regarding the efficiency of foliar intake, it would appear that the plant burden produced by soils containing long term deposits is several orders of magnitude greater than that which could be transferred from foliar interception of trace elements in the atmosphere. Soil concentrations are the result of accumulation of elements over the long-term, and crops raised in these soils tend to concentrate the trace elements in the plant tissue. By contrast, the foliar intake rate can be no greater than the deposition rate on the plant surface, and there is much uncertainty regarding the efficiency of the plant in absorbing the deposited particles. Thus, it is clear that the soil uptake scenario (Table 5-8) represents the more adverse case for plant uptake of trace elements. This scenario assumes no interference (e.g., animal or crop uptake) with trace element buildup in soils over a 40 year period, and a fixed concentration of elements in the soil despite crop uptake.

Trace element emissions also affect the quality of drinking water. The impact of trace element particle deposition on runoff water concentration will be related to the relative increase in soil concentration due to long term atmospheric deposition of elements. The actual runoff concentrations may be estimated by applying average sediment burden rates for representative runoff per unit of watershed area. The sediment is assumed to carry the cumulative deposits of metals originating from the boiler emissions. Table 5-10 summarizes estimates of increased soluble metals concentrations for runoff waters in the vicinity of the model plant. The estimated concentrations are substantially less than the standards for livestock drinking water and potable water. The concentration of lead is predicted to approach background concentrations in runoff water after 40 years of coal firing. However, hazard to human health by drinking water impacts appears remote.

IMPACT ON ECOLOGY

The ecological environment will be affected by air emissions and by solid waste residuals generated by air pollution control equipment.

Effects of Air Emissions

A major ecological impact category most likely to be affected by utility boiler emissions is plant life. Of the major gaseous pollutants emitted by fossil fuel combustion, plant life is most affected by SO_2 and NO_x in the concentration ranges expected. Concentrations of CO and hydrocarbons produced by coal firing of utility boilers would be expected to

TABLE 5-10. TRACE ELEMENT CONCENTRATION IN RUNOFF WATER IN VICINITY OF CONTROLLED COAL-FIRED UTILITY BOILER

Element	Typical Background Concentration of Soluble Metals In Runoff Water* mg/l	Increase In Soluble Metals Concentration In Soil After 40 years† mg/kg	Increase In Soluble Metals Concentration In Runoff Water‡ After 40 years mg/l	EPA Proposed Maximum Acceptable Concentration For Livestock mg/l	Standard As Critical Concentration In Potable Water mg/l
As	4×10^{-4}	9×10^{-3}	9×10^{-6}	2×10^{-1}	1×10^{-2}
Cd	1×10^{-4}	2×10^{-2}	2×10^{-5}	5×10^{-2}	1×10^{-2}
Cr	1×10^{-5}	8×10^{-7}	8×10^{-10}	1	2×10^{-2}
Ni	1×10^{-4}	1×10^{-5}	1×10^{-8}	---	5×10^{-2}
Pb	7×10^{-4}	3×10^{-1}	3×10^{-4}	1×10^{-1}	1×10^{-2}
Zn	3×10^{-3}	2×10^{-1}	2×10^{-4}	25	5×10^{-2}

*Based on average soil particulate runoff rate of 1000 mg/l of runoff water, and soluble endogenous concentration of metals in soils (15).

†Based on increase in trace element concentration (Table 5-7) and solubility of elements (Table 5-8).

‡Based on average soil particle runoff rate of 1000 mg/l of runoff water, and increased soluble metals concentration in soil after 40 years.

cause negligible impact on vegetation (4, 18). The maximum levels of NO_x and SO_2 expected to occur in the vicinity of utility boilers are near or exceed the threshold injury values for these pollutants. Sensitive plants in the vicinity of the utility boiler could suffer injury, although such injury would be limited to a downwind sector a few miles from the plant.

The secondary pollutants (ozone and peroxyacytylnitrates) formed by reaction of hydrocarbons and nitrogen oxides are considerably more toxic than either of the precursors alone. The formation of secondary compounds in boiler stack plumes and the impact of the boiler nitrogen oxides emissions on urban photochemical smog depend on complex relationships which are not yet totally understood. Therefore, it is not possible to reliably estimate the effect of NO_x emissions levels on levels of photochemical compounds. However, based on typical regional emissions figures, it appears that emissions from power plant fuel combustion provide a significant source of the regional emissions of NO_x necessary for photochemical smog. Approximately 28% of the nation's NO_x emissions are produced by combustion in power plants (19).

If NO_x emissions from utility boilers are a significant contributor to photochemical smog, then there is valid concern that boiler emissions may contribute to plant injury. The effects of photochemical air pollution on plant life have been observed frequently at various different severities throughout the United States. In addition, the effect of the major constituents of photochemical smog (products of nitrogen oxides and organic compounds) on plants has been investigated separately. The pigmentation of small areas of palisade cells is characteristic of ozone injury, and a bronzing of the undersurface of leaves is typical for peroxyacytylnitrate injury. Table 5-11 illustrates the relatively low levels of ozone which will produce significant plant injury to crops. The concentrations shown are typical of many areas experiencing photochemical air pollution, and suggest the necessity for concern over sources emitting high levels of NO_x.

Nitrogen oxides may also cause injury to vegetation by direct contact. The significant oxides of nitrogen are NO and NO_2. The major oxide in combustion emissions is NO. However, after residence in the atmosphere, NO is

TABLE 5-11. PROJECTED OZONE CONCENTRATIONS WHICH WILL PRODUCE, FOR SHORT TERM EXPOSURES, 20 PERCENT INJURY TO ECONOMICALLY IMPORTANT VEGETATION GROWN UNDER SENSITIVE CONDITIONS*

	Concentrations producing injury in three types of plants, ppm		
Time, Hr	Sensitive	Intermediate	Resistant
0.2	0.40-0.90	0.80-1.10	1.00 and up
0.5	0.20-0.40	0.35-0.70	0.60 and up
1.0	0.15-0.30	0.25-0.55	0.50 and up
2.0	0.10-0.25	0.20-0.45	0.40 and up
4.0	0.07-0.20	0.15-0.40	0.35 and up
8.0	0.05-0.15	0.10-0.35	0.30 and up

* Reference 20.

converted to NO_2 by photolysis and by photochemical interaction with hydrocarbons. The effect of NO_2 on plant life has been studied under controlled laboratory conditions. Acute injury is characterized by collapse of cells and subsequent development of necrotic patterns. Chronic injury, caused by exposure to low concentrations over long periods, is characterized by chlorotic or other pigmented patterns in leaf tissue. Such injury results in reduction of growth and reproduction. Only limited data are available to characterize the effect of NO on plants. Generally, it appears that NO leads to effects somewhat similar to those observed for NO_2, but at slightly higher threshold concentrations. Therefore, for worst case evaluations of the impact of ambient NO_x levels, it is assumed that NO_x exists as NO_2, and that the NO_x levels are not depleted by the photochemical reactions which typically occur in urban areas.

Figure 5-3 illustrates the threshold concentrations at which various degrees of damage result from exposure to NO_2. Based on the expected concentration of NO_x in the vicinity of the coal-fired utility boiler, and the assumption it is converted entirely to NO_2, it appears that acute leaf damage may be anticipated to occur as a result of short term plume trapping.

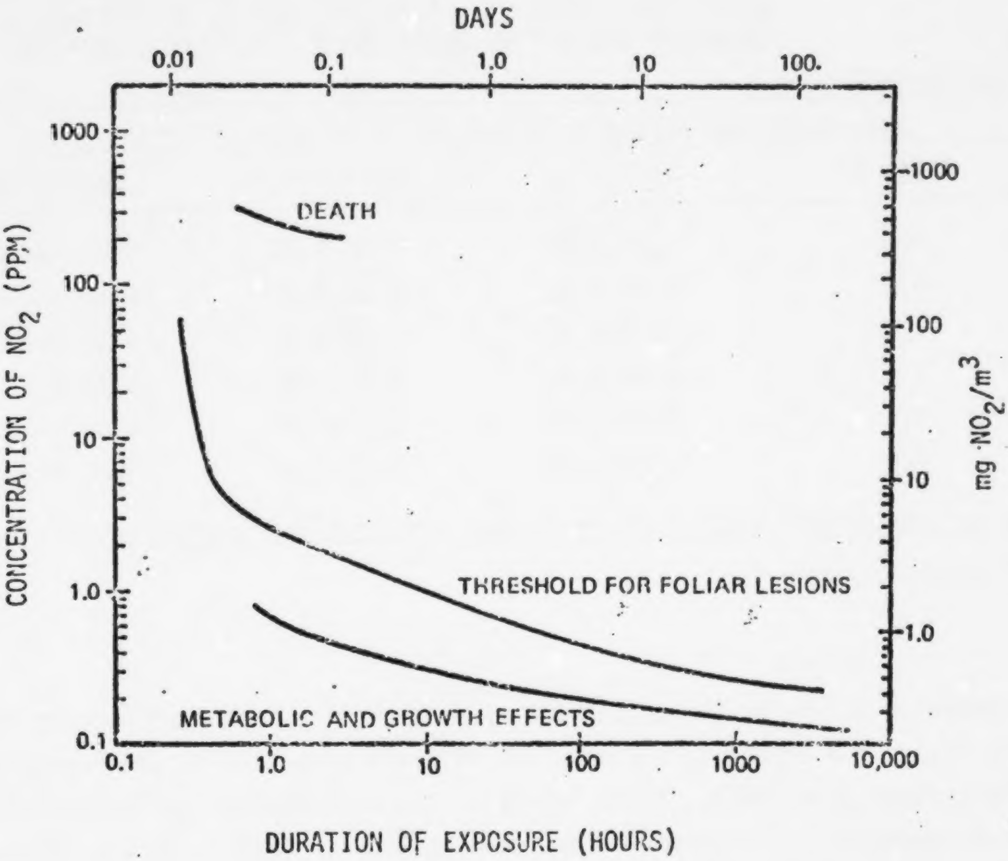

Figure 5-3. NO_2 threshold concentrations for various degrees of plant injury (21).

Chronic effects, including growth and yield reductions, may also be noticed over the long term. However, the extent of the damages would be localized within a few miles of the boiler, and would be expected to occur to those plants most sensitive to NO_2 injury (i.e., cotton, navel orange, spinach, etc.).

Acute short term injury to vegetation by SO_2 exposure is characterized by damaged leaf areas which first appear as water soaked spots, and later appear as bleached white areas or darkened reddish areas. Chronic SO_2 injury is usually characterized by chlorosis (yellowing) which develops from lower concentrations over extended periods of time. Either acute or chronic SO_2 injury may result in death or reduced yield of the plant if the extent of the damaged tissue exceeds 5 to 30 percent of the total amount of foliage.

The impact of the expected SO_2 concentrations varies with the plant species. Threshold injury in sensitive plants may be caused by short term SO_2 levels as low as 30 $\mu g/m^3$ (22). Table 5-12 summarizes the broad categories of sensitivity for different plants. Grain, vegetable, pasture, and forage crops are susceptible to SO_2 damage for most of the growing season. These crops may suffer yield reductions in areas where power plants such as that of the present study are located, although the damage would be relatively localized. Data presented in Figure 5-4 indicate that peak SO_2 concentrations expected to occur near the coal-fired boiler may possibly cause leaf damage to occur in the more sensitive plant species.

It should be noted that the plant damage thresholds illustrated by Figure 5-4 apply to conditions of temperature, humidity, soil moisture, light intensity, nutrient supply, and plant age which cause maximum susceptibility to injury. The occurrence of such conditions are rare. In fact, in the unlikely event that all such conditions are met, the dose-response curves indicate that plant injury could occur without a violation of the federal air quality standard for the 3 hour or 24 hour concentration of SO_2. Additional susceptibility may also result from synergistic effects of sulfur dioxide and other pollutants. Particularly relevent to the urban environment are combinations of sulfur dioxide and ozone. Moderate to severe injury of tobacco plants have been observed for four hour exposures to concentrations of 0.1 ppm (262 $\mu g/m^3$) SO_2 in combination with 0.03 ppm ozone. Because high ozone levels are a frequent problem in the vicinity of urban areas, susceptibility to plant injury by SO_2 pollution is greater when utility boilers are also sited in urban areas. One of the major concerns associated with fossil fuel utilization is acid precipitation resulting from wet deposition of suspended sulfur and nitrate compounds. Data

TABLE 5-12. SENSITIVITY OF COMMON PLANTS TO SO_2 INJURY*

Vegetation			Crops		
Sensitive	Intermediate	Resistant	Sensitive	Intermediate	Resistant
White pine	Maple	Sugar maple	Alfalfa	Irish Potato	Corn
Goldenrod	Virginia creeper	Phlox	Barley	Clover	Sorghum
Cottonwood	White oak	Oak	Oats	Sweet clover	
Virginia creeper	Elm	Maple	Rye		
Aster	Shortleaf pine	Shrubby willow	Wheat		
Gooseberry	Aster		Sweet potato		
Elm	Linden		Soybean		
Wild grape			Sweet clover		
American elm			Cotton Tobacco		
White ash			Clover		
Virginia pine					
Tulip tree					

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* Reference 23.

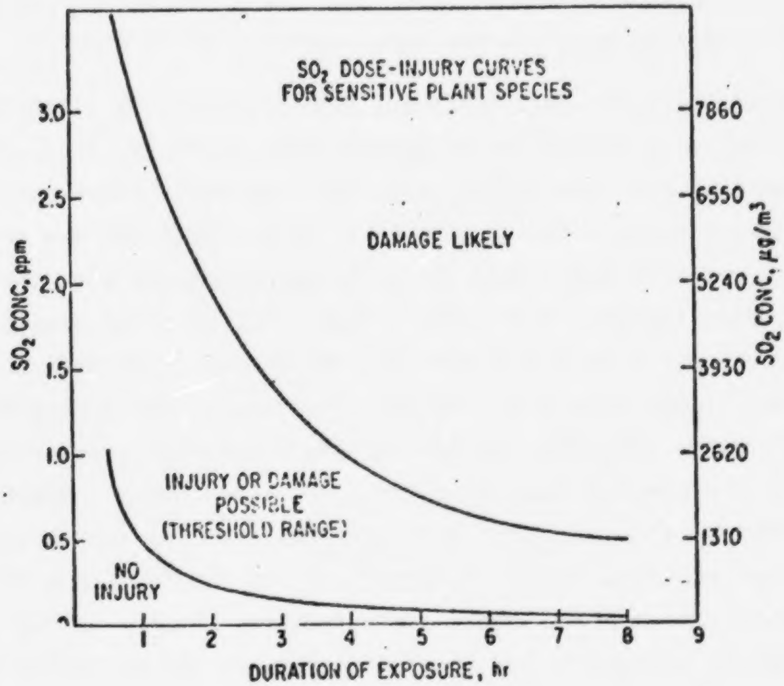


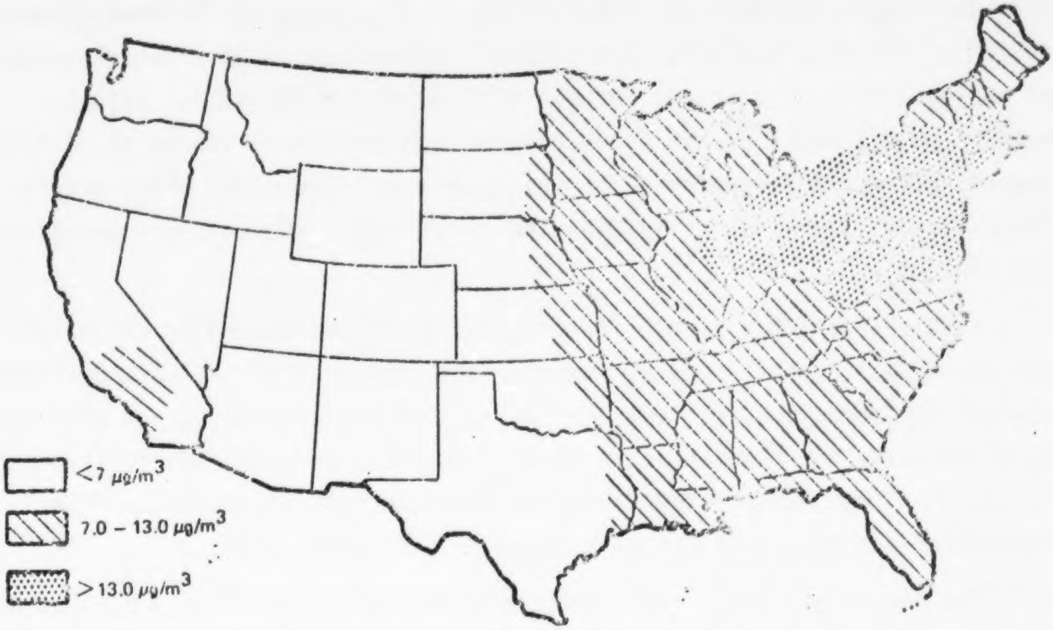
Figure 5-4. SO_2 dose-injury curves for sensitive plant species (22).

show that there has been an intensification of acidity in the northeastern region of the U.S. since the mid 1950's. Precipitation in a large portion of the eastern U.S. averages between pH 4.0 and 4.2 annually. Values between pH 2.1 and 3.6 have been measured for individual storms at distances several hundred miles downwind of urban centers. The areas experiencing highest acidity are typically downwind of the areas where sulfur emissions are highest (17, 21).

Acid rain affects plant life in varying degrees depending on the pH and the type of plant species. Experiments show that the effects on plants may include reduction in growth or yield, leaf damage, death, and chlorosis. Acid rain also has been shown to affect aquatic organisms, and it is believed that thousands of lakes are now experiencing reductions in fish population due to acidification between pH 5.0 and 6.0 (21).

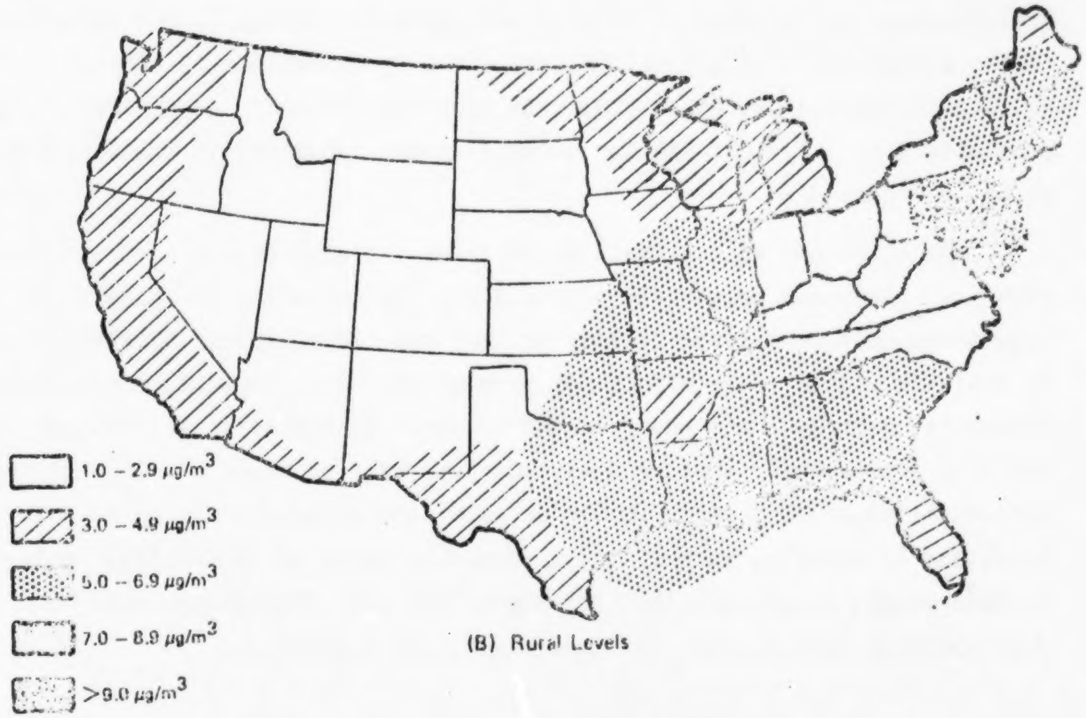
The impact of fossil fuel combustion in controlled utility boilers on acid precipitation and plant damage is potentially significant. In the previous discussion, it was estimated that controlled coal-fired boilers could account for a level of 11.0 $\mu g/m^3$ suspended sulfate in the central region of the U.S. This level is approximately equivalent to ambient sulfate concentrations associated with areas experiencing significant acid precipitation. Typical ambient sulfate levels prevalent in the U.S. are shown in Figure 5-5 .

Vegetation may also sustain injury from elevated levels of trace elements. As shown previously (Table 5-9), concentrations of cadmium in vegetation near coal-fired utility boilers may exceed levels observed to be toxic in plants. The effects of cadmium toxicity in plants are wilting, chlorosis, necrosis, and reduction of growth. Substantial declines in yield of the soybean, wheat and lettuce have been observed when the tissue concentration of cadmium in foliar parts of these species was as low as 7, 3, and 11.5 mg/kg, respectively. Based on tests of the utility boiler of this study, it appears that emissions from coal firing may result in high cadmium plant burdens and potential plant injury.



<7 μg/m3
7.0 – 13.0 μg/m3
>13.0 μg/m3

(A) Urban Levels



1.0 – 2.9 μg/m3
3.0 – 4.9 μg/m3
5.0 – 6.9 μg/m3
7.0 – 8.9 μg/m3
>9.0 μg/m3

(B) Rural Levels

Figure 5-5. Geographical distribution of typical sulfate levels in the United States (23).

Effect of Solid Wastes

A major environmental concern involving the use of fossil fuels is the generation of coal ash and flue gas desulfurization (FGD) sludges. The quantity of such wastes depends on the proportion of coal utilization and the amount of SO_2 removed from stack gases. It has been estimated that by 1985 coal ash will be generated at a rate of 83 Tg/y and FGD sludges at a rate of 30 Tg/y (dry basis). Landfill is the common means of disposal for these wastes. By 1980, it is estimated that 2000 to 3000 m^2 of land per MW of boiler capacity will be required for disposal purposes (24). The composition of the wastes will depend on the fuel source, the boiler design, and the flue gas desulfurization system. Most FGD processes generate a waste sludge consisting predominantly of calcium sulfite and sulfate. Various trace elements are also found in the FGD sludge. The trace elements originate from reagents used in SO_x removal, from process water, from trace elements in the combusted coal, and from fly ash which is collected by the FGD system. Fly ash and bottom ash usually consist of about 80 percent silica, alumina, iron oxide, and lime. The composition of trace elements found in bottom and fly ash is similar.

Based on tests of the coal-fired boiler, the rate of generation of solid waste from a 874 MW coal-fired boiler would be 0.11 Gg/hr of bottom slag/fly ash and 0.13 Gg/hr of scrubber sludge from the FGD operator.

The concentrations of trace elements in the combined fly ash/bottom slag and in the scrubber sludge are shown in Table 5-13 and 5-14. For almost all elements, the concentrations far exceed both the health and ecological DMEG values for both solids. The waste is considered hazardous, creating difficult waste disposal problems.

FGD scrubber wastes and coal ash are usually disposed in impoundment ponds or landfills. The major concern in either disposal approach is the release of trace elements to ecosystems in localized areas surrounding the disposal sites. Lateral and upward movement of trace elements through the soil to plant rooting zones may be possible, and contamination of ground and surface waters may occur. Additional adverse consequences include the diversion of land from other uses, and aesthetic degradation at the disposal site.

TABLE 5-13. TRACE ELEMENT CONTENT OF FLY ASH AND BOTTOM SLAG FROM COAL FIRING

Element	Concentration mg/kg	DMEG value, mg/kg		Discharge Severity	
		Health	Ecology	Health	Ecology
Al	82,000	16,000	200	5.1	410
As	11	50	10	0.21	1.1
Be	8.2	6	11	1	0.75
Ca	66,000	48,000	3,200	1.4	21
Cd	1.2	10	0.2	0.12	6
Co	44	150	50	0.29	0.88
Cr	210	50	50	4.2	4.2
Cu	820	1,000	10	0.82	82
Fe	170,000	300	50	580	3,500
Hg	< 1	2	50	< 0.5	< 0.02
Mg	ND*	18,000	17,400	---	---
Mn	700	50	20	14	35
Ni	330	45	2	7.3	200
Pb	160	50	10	3.2	16
Sb	7.0	1,500	40	0.0047	0.17
Sr	280	9,200	ND†	0.03	---
V	86	500	30	0.17	2.9
Zn	1,500	500	20	3.0	75

---

[*] Level 2 procedures were utilized.

[†] ND - data not available.

TABLE 5-14. TRACE ELEMENT CONTENT OF SCRUBBER DISCHARGE SOLIDS FROM COAL FIRING

Element	Concentration mg/kg	DMEG value, mg/kg		Discharge Severity	
		Health	Ecology	Health	Ecology
Al	24,000	16,000	200	1.5	120
As	110	50	10	2.2	11
Be	2.5	6	11	1	0.22
Ca	51,000	48,000	3,200	1.1	16
Cd	36	10	0.2	3.6	200
Co	22	150	50	0.15	0.44
Cr	52	50	50	1.0	1.0
Cu	190	1,000	10	0.19	19
Fe	50,000	300	50	170	1,000
Hg	< 1.0	2	50	< 0.5	< 0.02
Mg	0.49	18,000	17,400	0.000027	0.000028
Mn	560	50	20	11	28
Ni	96	45	2	2.1	5
Pb	1,100	50	10	22	110
Sb	38	1,500	40	0.025	0.95
Sr	990	9,200	ND[†]	0.11	--
V	190	500	30	0.38	6.3
Zn	6,500	500	20	13	320

[*] Level 2 procedures were utilized.

[†] ND - data not available.

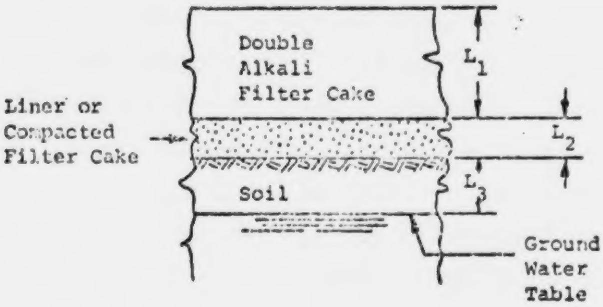
Because of the limited experience concerning land disposal of wastes, and the long time lags preceding future potential adverse impacts, there is significant uncertainty regarding the level of restrictiveness necessary to assure the environmental adequacy of various land disposal methods. Because of such uncertainty, it seems likely that stringent waste disposal regulations will be proposed to prevent the migration of waste sludges in the terrestrial environment and the movement of leachate to underground water sources.

Disposal of FGD sludges and coal ash is already subject to regulations at the state level. Recent federal legislation (the Resource Conservation and Recovery Act) now requires that criteria be developed to classify wastes and suitable disposal management techniques. Under the proposed criteria it is plausible that FGD sludges and coal ash may be classified as hazardous waste, and that disposal of these wastes will be restricted by the stringent requirements now being proposed for hazardous waste management facilities. Typically, these requirements would restrict the land disposal of hazardous wastes to "secure landfills" designed to provide protection for all-time of the quality of ground and surface waters. By definition, the secure landfill would prevent significant adverse impact to certain environmental sectors (i.e., public health and ecology). Unfortunately, the secure landfill, is, by definition, an ideal design which cannot be attained except at very great cost. There is, therefore, a need to define reasonably attainable land disposal designs which offer a high level of environmental protection.

Various recent efforts have been conducted to define appropriate landfill criteria. In one pertinent study (25), the effectiveness of three scenario landfill designs for the disposal of FGD scrubber cake were evaluated. The scrubber cake considered is that generated by the Double Alkali FGD system utilized at the reference industrial boiler of this study. Migration of leachate to the groundwater and the loading rate of dissolved solids into the groundwater were estimated by considering the permeability of the landfill layers and the solubility of solids as determined from laboratory tests. Table 5-15 summarizes the analysis of the three landfill cases. As indicated, permeability of the soils and the scrubber waste is

TABLE 5-15. LEACHING RATES FOR THREE LANDFILL DESIGNS

Case	L_1 (m)	L_2 (m)	L_3 (m)	K_1 (m/sec)	K_2 (m/sec)	K_3 (m/sec)	K_{eff} (m/sec)	t_1 (years)	t_2 (years)	Q_s2 (kg/m^2/yr)
I	5.5	0.6	3.0	10^{-7}	10^{-10}	10^{-6}	7.7×10^{-8}	1	20	5.08
II	5.5	0.6	3.0	10^{-7}	10^{-8}	10^{-10}	1.5×10^{-10}	200	6000	0.016
III	6.1	0.3	3.0	10^{-7}	10^{-11}	10^{-6}	3.0×10^{-10}	100	3000	0.032


Double
Alkali
Filter Cake
Liner or
Compacted
Filter Cake
Soil
L_1
L_2
L_3
Ground
Water
Table

L_1 = Depth of uncompacted filter cake (m)

L_2 = Depth of compacted filter cake or liner (Case III) (m)

L_3 = Depth of soil (m)

K_1, K_2, K_3 = Coefficients of permeability of layers 1, 2, and 3, respectively (m/sec)

K_{eff} = Effective permeability of overall filter cake plus soil layers (m/sec)

t_1 = Time for migration of leachate to groundwater table (years)

t_2 = Time for washout of major dissolved solids from filter cake (years)

Q_s = Loading rate of total dissolved solids to groundwater (kg/m^2/yr) the primary factor in initiating leachate migration. In the first case, all net precipitation becomes leachate, and the time to reach groundwater is about one year while the time to wash out the major portion of the soluble solids is about 20 years. The overall washout rate of soluble solids during the 20 year period is calculated to be 5.08 $kg/m^2/yr$. Contamination of groundwater sources over significant landfill areas at this washout rate is clearly unacceptable. In the second and third cases, 200 and 100 years elapse before leachate reaches groundwater, and leaching of soluble substances occurs at the low loading rate of 1.6×10^{-2} $kg/m^2/yr$ and 3.2×10^{-2} $kg/m^2/yr$, respectively. The time for total washout of all soluble solids would be 6000 and 3000 years, respectively. The extent of impact of such a leaching rate would depend on the size of the landfill and the flow of the underground aquifer. For example, for case II, a 1 acre landfill over a small underground water source flowing at one million gallons per year would cause an increase of 2 ppm in the dissolved solids content of the underground water. Most of the 2 ppm increase would be composed of lime and sodium sulfate and sulfite salts. As indicated by Tables 5-13 and 5-14 trace element would comprise a small fraction of the incremental increase, and considering the low solubility of the trace elements, their concentration in the underground water would be at least three orders of magnitude less than the lime, sulfate, and sulfite concentrations, and well below the standard for potable water (see Table 5-10). The rate of leaching can be minimized still further by mixing bentonite with a layer of soil to provide a layer over the filter cake after it has been landfilled to the desired level. The bentonite soil mixture achieves a low permeability of 10^{-11} m/sec. By contrast, the permeability of silty clay and permeable soils is about 10^{-10} m/sec, and 10^{-6} m/sec, respectively. The permeability of the double alkali scrubber cake is 10^{-7} m/sec, whereas it is about 10^{-6} m/sec for lime/limestone type scrubber sludges.

Estimated leaching rates can be confirmed by tracking the migration of leachate in the landfill. In one experimental landfill used for disposal of FGD scrubber wastes (25), and which contains no seal or barrier other than the native clay silt (permeability of 10^{-8} m/sec), tests show that no leachate has migrated as far as six inches below the disposal layer after the first year of operation. The results and analyses indicate that landfills of untreated scrubber cake can be constructed such that significant adverse impacts will not occur. Moreover, it is conceivable that a completed landfill can be reclaimed for use as a park or farmland, provided a sufficient soil cover is applied and care is exercised not to disrupt the stabilized waste or to permit its migration entry into the terrestrial environment.

The environmental concerns associated with the wastewater holding and settling ponds for the fly ash/bottom slag and scrubber sludges are similar to those of the landfill operation. Leaching of water soluble constituents of the wastewater into the underlying soil, and into the groundwater, can occur. In one study (26) of the leachability of trace elements from ash and scrubber sludge settling ponds, samples of leachate from five different coal-fired generating stations were found to contain concentrations of trace elements exceeding proposed EPA standards for Public Water Supply Intake. The rate of leakage is affected by the type of element, soil type, and depth of water table. To prevent leakage, settling ponds are often lined with impervious material. As with landfills, evidence has shown that the absorption capacity of impervious soils can reduce concentrations of elements in the leachate before reaching the water table (26). With proper design of the settling ponds, it is expected that the impact of leaching can be minimized to an insignificant degree. It is expected that such designs will become mandatory under rules established by the authority of the Resource Conservation and Recovery Act.

ECONOMIC IMPACT

The direct economic impacts associated with residuals of fuel combustion involve the costs of damages (or benefits) sustained when the residuals enter the environment. Second order economic impacts associated with the residuals involve the alterations that occur in employment, the tax base, energy prices, income, and land values due to the damages (or benefits) resulting from combustion residuals. The quantification of direct economic impacts involves the difficult task of ascribing economic values to environmental changes. Quantification of second order economic effects are yet more difficult because of gaps in knowledge which make it impossible to determine the complex relationships between cost and the numerous socioeconomic factors involved.

A number of ongoing energy related studies are attempting to develop sophisticated economic models which will predict the cost of environmental damages (6, 23, 27). The models address the cost of visibility reduction, health effects (morbidity and mortality), and certain second order effects. Utilization of the models requires substantial input data involving regional demography and emission source distributions. The models require further refinement and are currently under continuing development. The data base or scope of the present program did not permit the adaption and utilization of such models.

The extent of the economic impacts resulting from residuals of coal-fired utility boilers is proportional to the extent of the environmental damages which occur. The analyses have shown that the impact of emissions from coal-fired boilers tested in this study is substantial. Ambient concentrations of gaseous pollutants and trace elements are estimated to be significant in the vicinity of the model coal-fired boiler. In fact, based on the worst case circumstances assumed for the analysis of maximum ambient concentrations, federal ambient air quality standards for sulfur oxides may be violated in the vicinity of the plant. Trace element concentrations in soils (i.e., especially cadmium) near coal-fired boilers may result in toxic accumulation of these elements in plants. Localized crop damage will be significant, and additional land requirements will be required at coal-fired plants for disposal of wastes. The cost of these impacts will be significant in the affected areas. Higher medical costs and loss of productivity will be experienced in the area of coal firing. Annual cost of cleanup and maintenance for soiling damages will be greater in the affected areas, revenue for crop sales will be reduced somewhat, and esthetic blight in the area of landfills will diminish the value of land and activities nearby.

Whatever the extent to which additional controls may be required for coal-fired boilers, the comparative cost of such controls will probably be significant compared to the overall operating cost of a boiler and other factors affecting the overall costs. Control of NO_x emissions from cyclone-fired units would probably require either thermal decomposition or catalytic reduction; the cost of these technologies is rather uncertain at this time.

Costs of NO_x control for these units may be on the order of those for SO_x control. Even when predicted pollutant loadings meet environmental standards, it is not entirely clear whether the increasing use of fossil fuels may be continued at the forecasted levels of control technology without potential long term environmental damages. If it is found that long term effects of pollution (e.g., trace metals accumulation, lake acidity, land use) are unacceptable, then more stringent environmental regulations can be expected, and it is clear that energy costs will increase with increasing control requirements.

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APPENDIX A

SIMPLIFIED AIR QUALITY MODEL

Simple ambient air quality models were used to estimate the maximum expected ground level concentrations of criteria pollutants. It is important to recognize that these air quality values are estimates only, based upon simplifying assumptions, as discussed below. Two sets of meteorological conditions were considered: worst case and typical. Conditions were selected that are representative of what could reasonably be expected to occur almost anywhere in the country but are not specific to the area of the plant from which the pollutant emission rates were obtained. It was assumed that all species were inert. No photochemical reactions were considered.

There are several meteorological conditions which can produce high ground level pollutant concentrations. These conditions can result in plume coning, looping, fumigation, and trapping, all of which can cause high ambient concentrations. In the case of coning, high levels occur along the plume centerline. Looping causes high ground level concentrations at points where the plume impacts the ground. Fumigation causes high ground level concentrations which are generally lower than those from plume trapping. For this study it was assumed that plume trapping constituted the worst case in terms of ground level concentrations.

Trapping conditions occur when an inversion layer or stable air aloft inhibits upward dispersion of the plume. Although the plume is trapped by the capping stable layer at height L, the plume distribution is still Gaussian in the horizontal and uniform in the vertical directions. Ambient concentrations can be estimated by the following equation (1):

$$X\ (x,0,z;H) = \frac{Q}{2\pi u\sigma_y\sigma_z}\left\{\exp\left[-1/2\left(\frac{z-H}{\sigma_z}\right)^2\right] + \exp\left[-1/2\left(\frac{z+H}{\sigma_z}\right)^2\right] + \sum_{N-1}^{J}\left[\exp -1/2\left(\frac{z-H-2NL}{\sigma_z}\right)^2 + \exp -1/2\left(\frac{z+H-2NL}{\sigma_z}\right)^2 + \exp -1/2\left(\frac{z-H+2NL}{\sigma_z}\right)^2 + \exp -1/2\left(\frac{z+H+2NL}{\sigma_z}\right)^2\right]\right\} \tag{1}$$

Where: $X\ (x,y,z;H)$ = Concentration at point (x,y,z) assuming an effective stack height of H, $\mu g/m^3$

H = Effective stack height, m

Q = Pollutant emission rate, kg/hr

μ = Mean wind speed, m/s

σ = Concentration distribution within the plume in the horizontal (σy) and vertical (σz) directions, m

z = Height above the ground, m

J = Maximum wind speed class index, unitless

N = Wind speed class index, unitless

L = Height of the stable layer, m

At ground level ($z = 0$) and at the plume center line ($y = 0$) Equation (1) reduces to:

$$X\ (x,0,0;H) = \frac{Q}{\pi u\sigma_y\sigma_z}\left\{\exp\left[-1/2\left(\frac{H}{\sigma_z}\right)^2\right] + \sum_{N=1}^{J}\left[\exp -1/2\left(\frac{H+2NL}{\sigma_z}\right)^2 + \exp -1/2\left(\frac{H-2NL}{\sigma_z}\right)^2\right]\right\} \tag{2}$$

For typical conditions, ground level concentrations were calculated using a Gaussian solution to the convective diffusion equation (2):

$$X\ (x,y,o) = \frac{Q}{\pi\sigma_y\sigma_z\bar{\mu}_s}\exp -\left\{(H^2/2\sigma_z^2) + (y^2/2\sigma_y^2)\right\} \tag{3}$$

where X = Concentration, g/m^3
Q = Pollutant release rate, g/s
σ_y, σ_z = Crosswind and vertical plume standard deviations, m
$\bar{\mu}_s$ = Mean wind speed, m/s
H = Effective stack height, m
x,y = Downwind and crosswind distances, m

At the plume centerline, Equation (3) reduces to:

$$X\ (x,o,o) = \frac{Q}{\pi \sigma_y \sigma_z \bar{\mu}} \exp - \frac{H^2}{2\sigma_z^2} \tag{4}$$

The maximum value of this equation occurs at the distance where $\sigma_z = H / \sqrt{2}$.

In Equations (3) and (4), H is defined by:

$$H = H_s + \Delta H \tag{5}$$

Where H_s = physical height of the stack and H = plume rise, both expressed in meters. There are more than 30 plume-rise formulas in the literature. All of which require empirical determination of one or more constants. For the purpose of this study, the Briggs plume rise formula was chosen to calculate the final plume rise in stable conditions,

$$\Delta H = 2.6 \left(\frac{F}{\mu s} \right)^{1/3} \tag{6}$$

Where: ΔH = Plume rise, m
μ = Wind speed, m/s
s = Stability parameter, unitless
F = Buoyancy flux.

The stability parameter, s, is defined as:

$$S = \frac{g}{\Theta} \frac{\partial \theta}{\partial z} \tag{7}$$

Where: g = Gravitational constant, m/s^2;
Θ = Potential air temperature, K.
$\partial\theta/\partial z$ = $(\partial T/\partial z)$ + 0.0098 K/m, the potential temperature gradient. Based on the normal lapse rate, $\partial T/\partial z$, of temperature in the

atmosphere of -0.0065 K/m, a value of .0033 K/m was employed for $\frac{\partial \Theta}{\partial z}$ in this study.

The buoyancy flux, F, is defined as:

$$F = \frac{\Delta T}{T_s} gwr^2 \tag{8}$$

Where ΔT = Stack temperature minus the ambient air temperature, K
T_s = Stack temperature, K
g = Gravitational constant, m/s^2
w = Stack exit velocity, m/s
r = Inside radius of the stack, m.

The plume rise was calculated using Equation (6). The data used for the calculations are shown in Table A-1. The values selected for wind speed are discussed below.

TABLE A-1. STACK PARAMETERS AND PLUME RISE

Stack temperature, K	463
Ambient temperature, K	293
Stack exit velocity, m/s	33
Stack area, m^2	41
Stack height, m	213

Equation (2) was used to estimate maximum ambient concentrations resulting from short term meteorological conditions causing plume trapping. As a worst case estimate for this study, plume trapping conditions were assumed to persist for periods as long as three hours. Equation (4) was used to estimate maximum ambient concentrations for conditions which could typically persist over a 24 hour period. For the 24 hour concentration forecasts, typical conditions of wind speed (4 m/sec) and atmosphere stability (Class D stability) were assumed to persist. For the short-term plume trapping, conditions of low wind speed (1 m/sec) and a moderately unstable atmosphere (Class B stability) were assumed to persist throughout the applicable averaging period. These conditions were selected because they produce high ground level concentrations. The inversion inducing plume trapping was assumed to be at an elevation equivalent to the effective stack height (817 m). Results of these calculations are presented in Table A-2.

TABLE A-2. PREDICTED MAXIMUM AMBIENT CONCENTRATIONS OF CRITERIA POLLUTANTS

Pollutant	Pollutant Concentration, $\mu g/m^3$
24 hour period:	
NO_x	46
CO	≤ 34
SO_2	48
Particulates	5
Total organics	0.2
Plume trapping:	
NO_x	2800
CO	≤ 2100
SO_2	2900
Particulates	310
Total organics	10

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APPENDIX B
ORGANIC ANALYSES FROM COAL FIRING

Sample Preparation

For coal firing, samples were prepared for both phases (Level 1 and 2) of organic analyses at the same time and aliquots were divided to meet the requirements of each phase. Runs 133 and 134 were made using the SASS train and were to supply all the organic samples. However, only 134 was prepared and fully analyzed because this sampling was taken when the facility was operating at a slightly higher percentage of capacity. The full data assessment, therefore, has been generated only for run 134 and is representative of organic emissions from this source.

The compound identification phase of this effort (Level 2) used gas chromatography/mass spectrometry (GC/MS) as the only analytical technique. Compounds of low volatility, high molecular weight or with a strong affinity to those GC columns used would not have been identified. Therefore, for this environmental assessment, closure with the Level 1 nonvolatile organics ($> C_{16}$) was not expected.

Samples were prepared using procedures detailed in Reference B-2 with modifications whenever required to ensure Level 2 quality data would be produced. The steps involved for each sample type are summarized below.

Water samples: Samples were taken on each of six sampling days at the site. Ten ℓ composites were prepared for each sample stream. Each composite was extracted three times with a total of 450 ml of methylene chloride at each of three pH levels. First the water was acidified to a pH of 2 with HCl; then it was neutralized to pH 7; and finally, it was made basic to pH 11 with NaOH.

XAD-2 module condensates: Each sample was extracted three times with methylene chloride at each of three pH conditions: 2, 7, and 11. The volume of methylene chloride used was 10 percent of the condensate volume.

Solids (filters and loose particulate): Each sample was extracted with methylene chloride in a Soxhlet apparatus for 24 hours.

XAD-2 resins: Each sample was extracted in a Soxhlet apparatus for 24 hours with methylene chloride.

Slurries: The solids and liquids were separated by filtration and a liquid composite was made for each stream to represent the total sampling period of six days. The water composite was extracted three times with a total of 450 ml of methylene chloride at each of three pH conditions. In this case, the pH was first adjusted to 11, then the water acidified to pH 7; and finally to pH 2. A portion of the solid composites was extracted in a Soxhlet apparatus for 24 hours with methylene chloride.

1 ml aliquots were taken of each methylene chloride extract for TCO and GC/MS analyses. Then the solutions were concentrated to 10 ml in Kuderna-Danish evaporators. Aliquots taken for analyses included 1 ml for TCO and GC/MS and 1 ml for GRAV/IR. The flow diagram in Figure B-1 shows the sample handling and analysis procedures used.

Summary

Level 1--

Table B-1 is a complete overview of Level 1 data generated from the SASS sampling, run 134, both into (IN) and out of (OUT) the scrubber. The resultant Level 1 weight data are tabulated under "Level 1 Data Assessment, 134 IN, $\mu g/m^3$ and 134 OUT, $\mu g/m^3$". These data have been compared to the most toxic MEG compound for that Level 1 reporting point. The Level 1 reporting points are C1-C6, C7-C17 and LC1-LC7. The C1-C6 and C7-C17 categories are organized by boiling point ranges and the LC1-LC7 are organized by column separation fractions. Table B-2 gives a general outline of the Level 1 reporting points.

The results of this Level 1 assessment, by MEG categories and DMEG concentrations are:

- The Level 1 reporting points which were identified for Level 2 based on the presence of low probability (not likely present under these source conditions) MEG compounds were C3, C5, C6, C9, C10, LC5, and LC6.

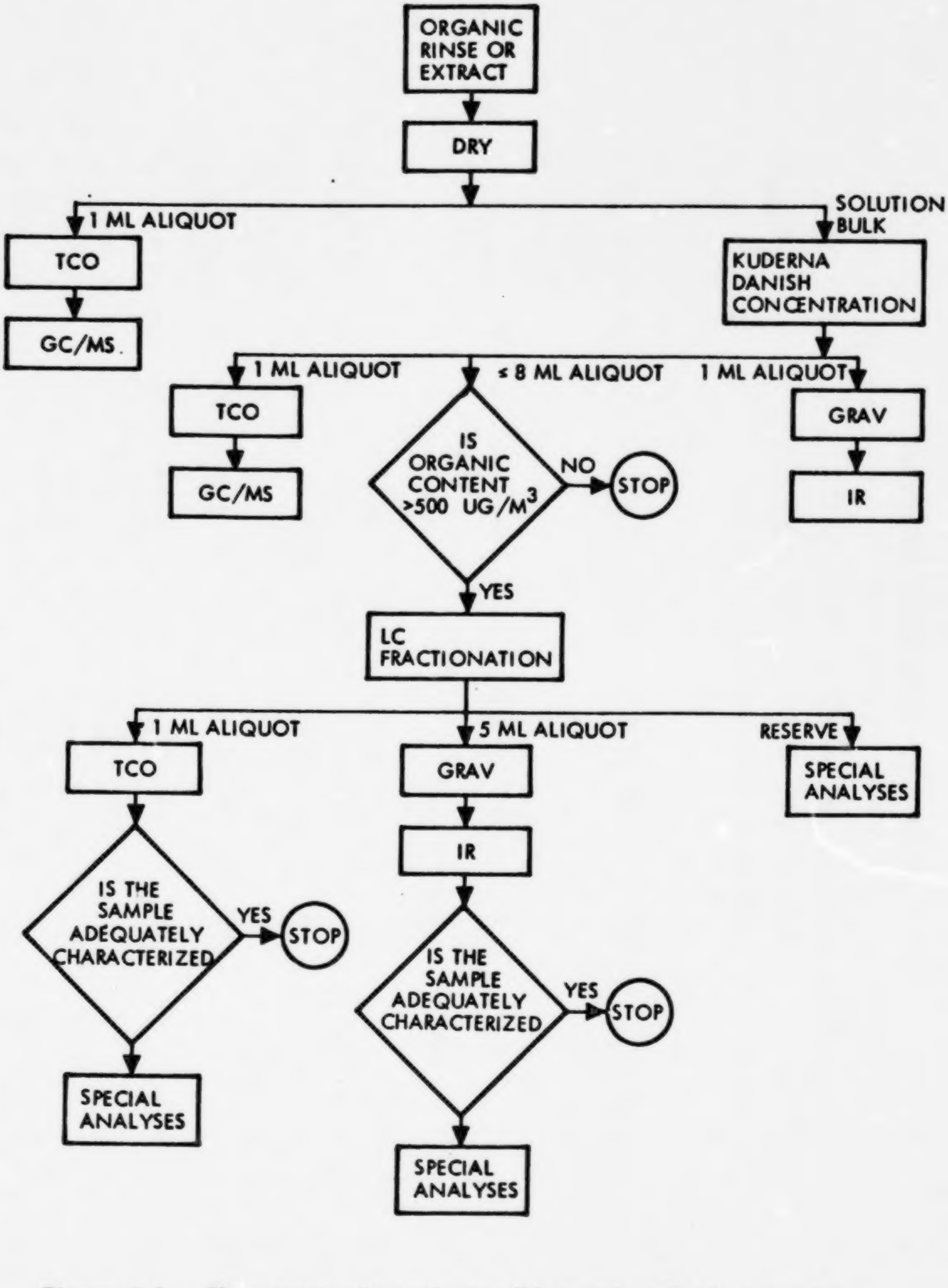
ORGANIC RINSE OR EXTRACT
DRY
1 ML ALIQUOT
SOLUTION BULK
TCO
GC/MS
KUDERNA DANISH CONCENTRATION
1 ML ALIQUOT
≤ 8 ML ALIQUOT
1 ML ALIQUOT
TCO
GC/MS
IS ORGANIC CONTENT >500 UG/M3
NO
STOP
GRAV
IR
YES
LC FRACTIONATION
1 ML ALIQUOT
5 ML ALIQUOT
RESERVE
TCO
GRAV
SPECIAL ANALYSES
IR
IS THE SAMPLE ADEQUATELY CHARACTERIZED
YES
STOP
IS THE SAMPLE ADEQUATELY CHARACTERIZED
YES
STOP
SPECIAL ANALYSES
SPECIAL ANALYSES

Figure B-1. Flow chart of sample handling and analysis procedures

TABLE B-1. LEVEL 1 DATA ASSESSMENT

	Level 1 Sampling Point	134 In g/m^3	134 Out g/m^3	Most Toxic MEG Compound	DMEG g/m^3	Probable MEG Category	Sample/DMEG		Assessment Notes
							134 In	134 Out	
C1-C6	C1	1.8x10^3	1.2x10^3	Methane	3.2x10^6	1. Aliphatic Hydro	<< 1	<< 1	Level 2 not required - Difference between IN and OUT within S&A accuracy.
	C2	< 6.5x10^2(< 1 ppm)	< 6.5x10^2	Acetylene	5.3x10^2	1. Aliphatic Hydro	<< 1	<< 1	
	C3	< 6.5x10^2(< 1 ppm)	< 6.5x10^2	Ethyleneimine	3.3x10^2	10. Amines	< 2	< 2	Most Toxic MEG compound is reactive - the nonreactive compound is a factor of 10 higher 6.5x10^2) Formaldehyde at 1.6x10^3). Level 2 required
	C4	7.4x10^2	6.5x10^2	Ethylamine	1.8x10^4	10. Amines	< 1	<< 1	Level 2 not required - Difference with IN and OUT within S&A accuracy.
	C5	< 6.5x10^2	< 6.510^2	Acrolein	2.5x10^2	7. Aldehydes/ Ketones	< 2.6	< 2.6	Most toxic MEG is reactive and ratio is within S&A uncertainty - next most toxic is Methyl Iodine at 8.5x10^2. Level 2 required.
	C6	< 6.5x10^2	< 6.5x10^2	N,N-Dimethyl-hydrazine	3.7x10	11. Azo Compounds	< 20	< 20	Most toxic MEG is reactive - next most toxic is dichloro-propenes at 1.1x10^4 Level 2 required.
	Total C1-C6	2.5x10^3 to 5.2x10^3	1.9x10^3 to 4.5x10^3						
C7-C16	C7			Tetramethyl Lead	1.5x10^2	26. Organo-Metallics			Solvent contaminants were the major cause of these concentrations.
	C8	4.7x10^2	2.3x10^2	Maleic Acid	1.0x10^3	8. Carboxylic Acids	0.5	0.2	
	C9	1.3x10	4.0x10	N-Nitroso-dimethylamine	1.2	12. Nitrosamines	10.0	33.0	Most toxic MEG is reactive - next most toxic is chloropyridine at 4.8x10^3 - IN and OUT within S&A uncertainty
	C10	2.6x10^2	1.9x10	N-Nitroso-diethylamine	1.2x10	12. Nitrosamines	22.0	1.5	Most toxic MEG is reactive - next most toxic is tribromomethane at 5.0x10^3
	C11	3.0x10^2	1.5x10	Hexachloro-cyclohexane	5.0x10^2	2. Halogenated Aliph. Hydrocarbons	0.6	0.03	Level 2 not required.
	C12	7.1x10	1.2x10	2,4-Dichloro-phenols	7.0x10^3	19. Halophenols	<< 1	<< 1	Level 2 not required.
	C13	7.4		Hexachloro-cyclo-pentadiene	1.1x10^2	2. Halogenated Aliph. Hydrocarbons	<< 1	<< 1	Level 2 not required.
	C14	2.4		Anisidines	5.0x10^2	10. Amines	<< 1	<< 1	Level 2 not required.
	C15	2.7x10	8.0x10^{-1}	4-Aminobiphenyl	4.5x10^3	10. Amines	<< 1	<< 1	Level 2 not required.
	C16	4.2x10	7.1	Phthalates	5.0x10^3	8. Carboxylic Acids and Esters	<< 1	<< 1	Level 2 not required
	Total C7-C16	1.2x10^3	3.3x10^3						

TABLE B-1 (Continued)

	Level 1 Sampling Point	134 In µg/m^3	134 Out µg/m^3	Most Toxic MEG Compound	DMEG µg/m^3	Probable MEG Category	Sample/DMEG 134 In	Sample/DMEG 134 Out	Assessment Notes
LC1-LC7	LC1	1.6x10	1.0x10	Tetraethyl Lead	1.0x10^2	26. Organometallics	<< 1	<< 1	Level 2 not required (IR identified aliphatic hydrocarbons.)
	LC2	6.3x10	3.0	Polychlorinated Biphenyls	5.0x10^2	16. Halogenated	1	1	Level 2 not required (IR identified aliphatic and aromatic hydrocarbons) POM screening necessary.
	LC3	2.4x10	9.0	Benzo(a)pyrene	2.1x10^{-2}	21. Fused Aromatic Hydrocarbons	1.1x10^3	4.3	Level 2 required for POM species.
	LC4	2.4x10^2	2.6x10	4-Nitrobiphenyl	1.3x10^3	17. Aromatic Nitro Compounds	1	1	Level 2 not required.
	LC5	1.0x10^3	6.2x10^2	n-Methyl-n-nitrosoaniline	1.3x10^3	12. Nitrosamines	0.77	0.5	Most toxic compound reactive - next most toxic Dinitrotoluene at 1.5x10^3 - Level 2 required (IR identified hydrocarbons, alcohols, esters and MEG.)
	LC6	5.7x10^2	2.0x10^2	Perchloromethyl-mercaptan	8.0x10^2	13. Mercaptans	0.71	0.25	Level 2 required.
	LC7	3.1x10^2	5.4x10	Pentachlorophenol 1-Aminonaphthalene	5.0x10^2 5.5x10^2	19. Halophenols 10. Amines	0.62 0.56	0.11 0.1	Level 2 required on 134 IN
	TOTAL LC1-LC7	2.2x10^3	9.2x10^2						
	TOTAL LC2+LC3+LC6	6.6x10^2	2.1x10^2						

TABLE B-2. GENERAL LEVEL 1 REPORTING POINTS

General Level 1 Sample Classes	Level 1 Reporting Point
Inorganics	• SSMS data in $\mu g/m^3$ for each element • Hg, As, Sb data in $\mu g/m^3$
Organics	• C1-C6 on site in $\mu g/m^3$ for each boiling point range • C7-C12 in $\mu g/m^3$ for each boiling point range • LC1-LC8 in $\mu g/m^3$ for each MEG category
LC Fraction	MEG Category Present (Theoretically Predicted Compounds)
1	1. Aliphatic Hydrocarbons (HCs) 2. Halogenated Aliphatic HCs
2	2. Halogenated Aliphatic HCs 15. Benzene, Substituded Benzene HCs 16. Halogenated Aromatic HCs 21. Fused Aromatic HCs 22. Fused Nonalternate Polycylic HCs
3	15. Benzene, Substituted Benzene HCs 16. Halogenated Aromatic HCs 21. Fused Aromatic HCs 22. Fused Nonalternate Polycyclic HCs 23. Heterocyclic Nitrogen Compounds

TABLE B-2 (Continued)

LC Fraction	MEG Category Present
4	3. Ethers 4. Halogenated Ethers 9. Nitriles 17. Aromatic Nitro Compounds 21. Fused Aromatic HCs 22. Fused Nonalternate Polycyclic HCs 23. Heterocyclic Nitrogen Compounds 25. Heterocyclic Sulfur Compounds
5	7. Aldehydes, Ketones 9. Nitriles 13. Mercaptans 17. Aromatic Nitro Compounds 18. Phenols 24. Heterocyclic Oxygen Compounds
6	5. Alcohols 7. Aldehydes, Ketones 8. Carboxylic Acids, Derivatives 9. Nitriles 10. Amines 18. Phenols 19. Halophenols

TABLE B-2 (Continued)

LC Fraction	MEG Category Present
7	18. Phenols 20. Nitrophenols
7	8. Carboxylic Acids, Derivatives 10. Amines 11. Azo Compounds, Hydrazine Derivatives
8*	8. Carboxylic Acids, Derivatives 14. Sulfuric Acid, Sulfoxides

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[*] Recent studies have shown that fraction 8 does not actually contain these theoretically predicted categories. Sulfuric acid and sulfoxides may not be removed from the samples by the original extraction process.

- The Level 1 reporting points which were identified for Level 2 by weight criteria only and did not have supportable infrared (IR) or low resolution mass spectral (LRMS) data to indicate that toxic species were present were LC5 and LC6.
- The Level 1 reporting point clearly requiring Level 2 analysis based both on high probability and IR and LRMS were LC2 and LC3 for the Halogenated Aromatic Hydrocarbons and the Fused Aromatic Hydrocarbons.
- For the C1-C7 species the Level 1 "IN" and "OUT" concentration variations are within the sampling and analytical accuracy. For reporting points C10, C11, C13, C15, C16, LC2, LC3, LC4 and LC7 the "OUT" concentrations are lower than the "IN" concentrations. Even though in most cases the "IN" concentrations do not exceed a DMEG criterion, the scrubber has reduced organic emissions.

Level 2--

Compounds identified and quantified have been organized on Table B-3 by Level 1 reporting points. This provides for some comparison with the Level 1 data.

An important analytical decision which was made when conducting this data evaluation was to remove from consideration and tabulation most of the common background compounds, e.g., phthalate esters, silicones and freons. Therefore, the data reported are adjusted for background variations except when a good deal of uncertainty existed.

The Level 2 effort identified unusual background contributions: in the C8 range, acetone condensation products; and in the LC2 and LC3 fractions, resin contributions. These are clearly identified on Table B-3.

The Level 2 analytical phase therefore:

- Verified that in the C1-C6 range, with good closure to the Level 1 data, the compounds emitted were not the most toxic for these reporting points. Those emitted did not exceed DMEG concentrations.
- Identified that the C8 and C9 species were condensation products of the SASS rinse solvents and not source related.
- Identified those Fused Aromatic Hydrocarbons and Aromatic Hydrocarbons required in LC2 and LC3 and those compounds identified as source emissions did not exceed DMEG concentrations.

In general the organic emissions were low and compounds did not exceed DMEG concentrations.

TABLE B-3. LEVEL 2 DATA ASSESSMENT

Level 1 Sampling Point	Level 2 Compound Identified	134 In µg/m^3	134 Out µg/m^3
C1	None		
C2	None		
C3	Dichlorofluoromethane		1.3×10^2
	Vinyl Chloride		8.0×10
C4	None		
C5	Methylene Formate		1.0×10^2
	Diethyl Ether	1.1×10^3	
	Carbon Tetrachloride		
C6	Tetrahydrofuran	1.8×10^2	1.8×10^2
	Methylmethacrylate	3×10^3	1.0×10^3
TOTAL C1-C6		4.3×10^3	1.5×10^3
C7	C7 Hydrocarbon	4.0×10	4.0×10
	Unsaturated Hydrocarbon	5.0×10^3	5.0×10^2
	Hydrocarbon	6.6×10^2	
C8	Toluene	1.1×10^3	
	Trichloroethylene	4.0×10^3	
	Methylisobutyl Ketone (Solvent Source)	2.5×10^3	4.0×10^2
C9	3-Methylene-2-pentanone (Solvent Source)	1.0×10^2	
C10	Trimethylbenzene	0.6	
C11			
C12			
C13			
C14			
C15			
C16			
TOTAL C7-C16		1.3×10^4	9.4×10^2

TABLE B-3 (Continued)

Level 1 Sampling Point	Level 2 Compound Identified	134 In μg/m^3	134 Out μg/m^3
LC1			
LC2	Phenyl (2,2,3-trimethyl cyclopentilidene) Methane	2.0	
LC3	4(2-Butenyl)-1,2-dimethylbenzene	3.0 x 10^{-1}	
	Decahydronaphthalene	1.0 x 10^{-1}	
	Di-tert-butylnaphthalene	3.0 x 10^{-1}	
	Dimethylisopropylnaphthalene	3.0 x 10^{-1}	
	Hexamethylbiphenyl	6.0 x 10^{-1}	
	Cyclohexylbenzene	3.0 x 10^{-1}	
	Hexamethyl, hexahydroindacene	3.0 x 10^{-1}	
	Trimethylnaphthalenylsilane	1.0	
	1,3-Diethylbenzene	2.0	
	C_6 Substituted Benzene	1.0	3.0 x 10^{-1}
	Dihydronaphthalene	3.0 x 10^{-2}	
	1,3,5-Triethylbenzene	3.0 x 10^{-1}	
	C_{10} Substituted Naphthalene	6.0 x 10^{-2}	
	C_{10} Substituted Decahydronaphthalene	1.0	
	Methylnaphthalene (2 isomers)	1.6	
	Anthracene or Phenanthrene	3.0 x 10^{-1}	
	1-1'-Biphenyl	4.0	
	9,10-Dihydrophenanthrene *or* 1-1'-Diphenylethene	2.0 x 10^{-1}	
	1,1-Bis (p-ethyl phenyl)-ethane or tetramethylbiphenyl (three isomers)	8.0	
	"Another" tetramethylbiphenyl 2-phenylnaphthalene	1.0	
	Tetramethylbenzene		< 3 x 10^{-2}
	5-Methylbenz-c-acridine	2.0 x 10^{-1}	
	2,6-Dimethyl-2,5-heptadion-4-one	1.0 x 10	
TOTAL Per LC3		2.3 x 10	
LC5	Phthalates		
	Benzoic Acid	Not Quantitated	Not Quantitated
	Aromatic Hydrocarbons		
	Butylacetate		3.0 x 10^{-1}
LC6	2,6-Piperiden-dione-4,4-dimethyl	2.0 x 10	
	Long Chain Acid; Methyl Ester	2.0 x 10^{-1}	
	2,3-Dimethyldecahydronaphthalene	< 3.0 x 10^{-2}	
	Ethylbenzaldehyde	4.0	3.0
	Dimethylbenzaldehyde	6.0 x 10^{-1}	
	2,4-Dimethylacetophenone		6.0 x 10^{-1}
	Trimethylcyclohexenone		1.0
	Nitric Acid Decylester		3.0 x 10^{-1}
TOTAL Per LC6		4.0 x 10	8.0
LC7	o-Methylbenzaldeoxime (C=N-OH)	Not Quantitated	
	Methyl Ester of Carboxylic Acid		3.0 x 10^{-1}
TOTAL LC2+LC3+LC6		6.5 x 10	8.3

Level 1 Data

Total Chromatographable Organics Analysis--

The gas chromatographic analyses (GC-TCO) were performed using either a Perkin-Elmer Sigma 1, a Varian 1860, or a Varian 5860 chromatograph with differential flame ionization detectors. The operating parameters were as follows:

- Column-10 percent OV-101 on Supelcoport, 100/120 mesh, 0.32 X 183 cm stainless steel.
- Temperatures-detectors, 300°C; injectors, 200°C; column, begin and hold at ambient for 5 min., then program temperature increase from 30°C to 250°C at 15°C/min.
- Flowrates-column, 30 mℓ/min. He; detectors, 300 mℓ/min air and 30 mℓ/min H_2.
- Electrometer-1 X 10^{-10} A/mV
- Recorder- 1 mV full scale
- Injections-1 μℓ.

These conditions provide a lower detectable limit of 0.7 ng/μℓ for n-alkanes. This is equivalent to a hydrocarbon concentration of 2 X 10^{-4} mg/m^3 in 30 m^3 of sample gas (the quantity of gas required in these tests) or 7 X 10^{-4} mg/ℓ in 10 ℓ of a water sample.

The instrument is calibrated so that results can be expressed in terms of the quantity of n-alkanes boiling in the temperature ranges shown in Table B-4. Calibration of the GC requires synthetic mixtures of the appropriate n-alkanes be chromatographed. A plot of retention times versus normal boiling points is then constructed, as illustrated in Figure B-2. The retention time intervals corresponding to the boiling points of interest are then determined graphically.

Quantitation of the peak areas on the chromatograms is based upon the instrument response to n-decane. A thorough description of the calibration is given in Reference B-2. Data reduction and quantitation of chromatograms obtained from the actual samples are done in two steps. First, all peak areas observed within the overall retention time interval of interest are added together. The total concentration of chromatographable organic

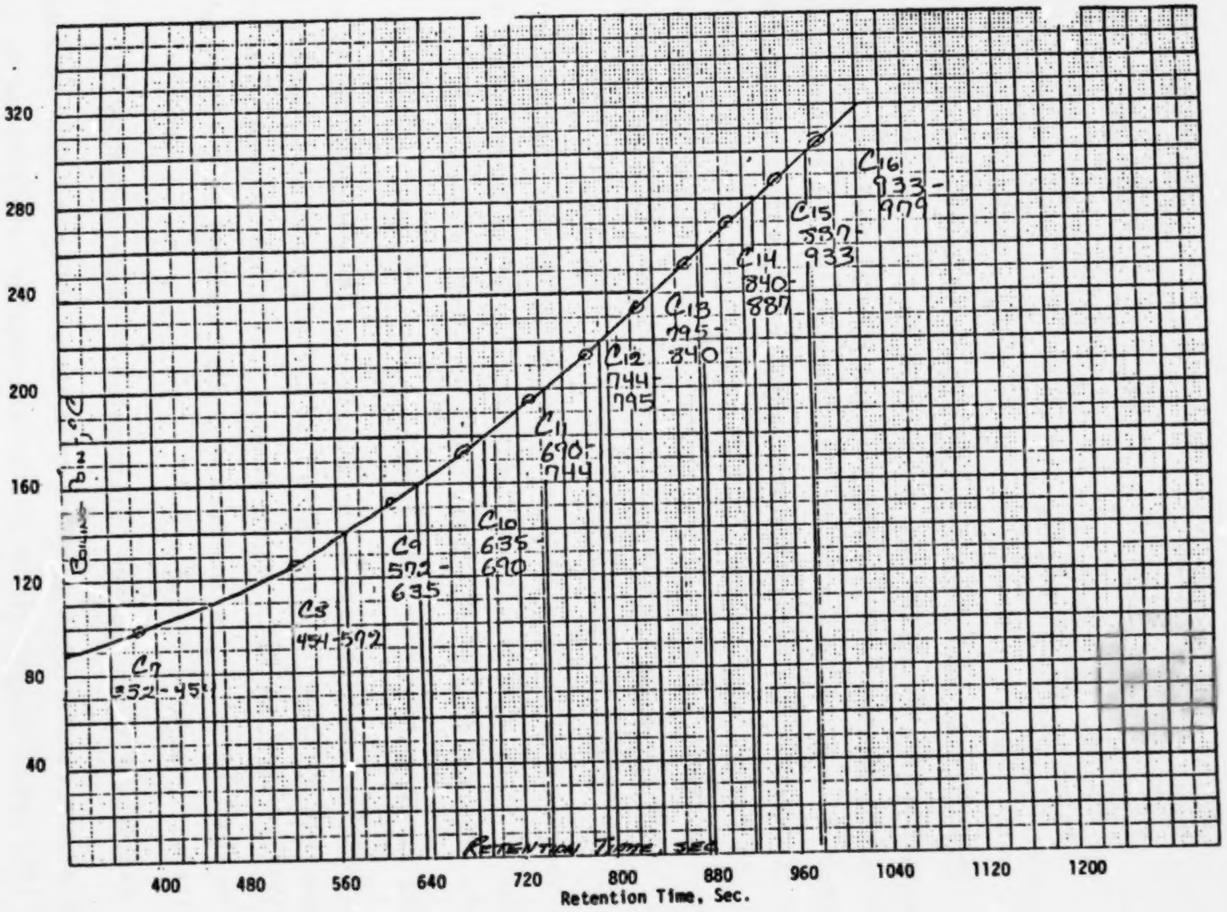


Figure B-2. Retention times versus boiling points for n-alkanes

TABLE B-4. BOILING RANGES OF n-ALKANES

C_7	90-110°C	C_{12}	200-220°C
C_8	110-140°C	C_{13}	220-240°C
C_9	140-160°C	C_{14}	240-260°C
C_{10}	160-180°C	C_{15}	260-280°C
C_{11}	180-200°C	C_{16}	280-300°C

material (TCO) in the sample is determined by dividing the total peak area by the sensitivity of n-decane and then multiplying by the appropriate dilution sample volume factors. Whenever the TCO is greater than 75 $\mu g/m^3$, the concentration of all peaks in each n-alkane equivalent boiling range fraction is determined. Peak areas are summed within each specific retention interval and the response factor for the corresponding n-alkane is used to determine the weight of material eluted from the GC. As before, the total amount of material in each sample is determined by multiplying the concentration by the sample volume and the fraction of sample extracted.

All samples were analyzed both prior to and after the Kuderna-Danish concentration step. The results of these C_7 - C_{16} analyses are given in Table B-5. (An explanation of sample codes is given in Table B-6.)

Gravimetry for C_{17} and Higher Hydrocarbons--

Gravimetric determinations were performed on the concentrates of solvent rinses and extracts in accordance with the procedure in Reference B-2: a one milliliter aliquot was taken from each sample and evaporated to dryness in an aluminum pan. The residues were then weighed on a microbalance. The results are presented in Table B-7.

Infrared Analyses (IR) on Samples Concentrated in Kuderna-Danish Evaporators--

Each of the concentrates weighing more than 0.5 mg was also scanned by infrared (IR) spectroscopy. After the final weighing, the residue in each weighing bottle was redissolved in methylene chloride and smeared onto a NaCl window. The resulting spectra and the compound classes whose presence was identified are summarized in Table B-8.

TABLE B-5. TCO OF SAMPLE CONCENTRATES AND NEAT SOLUTIONS

Sample	Hydrocarbon Content										
	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	Total
132/6-1-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-2-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-3-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-4-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-5-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-6L-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-6S-SE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/kg
132/6-7L-LE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-7S-SE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/kg
134-IN-CD-LE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-OUT-CD-LE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-PR-GC	-	1313	-	-	-	-	-	-	-	-	1313 μg/m³
134-OUT-PR-GC	-	507	44.2	-	6.1	-	-		-	1.1	558 μg/m³
134-IN-MR-GC	-	LB	-	-	-	-	-	-	-	-	0 μg/m³
134-OUT-MR-GC	-	-	-	10.5	-	-	-	-	-	-	10.5 μg/m³
134-IN-CYR-GC	-	7460	-	55.9	37.3	37.3	-	-	-	-	7590 μg/m³
134-IN-XR-SE-GC	-	-	-	-	52.7	39.5	-	-	-	-	92.2 μg/m³
134-OUT-XR-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-1C-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-3C-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-10C-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-PF-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-OUT-PF-SE-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
133-18-SE-GC	-	-	-	-	-	-	-	-	-	-	0 mg/kg
132/6-1-LE-KD-GC	-	-	-	-	-	0.02	-	-	-	<0.01	0.02 mg/l
132/6-2-LE-KD-GC	-	-	0.02	0.01	0.05	0.03	0.01	-	<0.01	0.02	0.14 mg/l
132/6-3-LE-KD-GC	-	-	-	-	0.04	0.01	-	-	<0.01	0.01	0.06 mg/l
132/6-4-LE-KD-GC	-	-	-	-	0.04	-	-	-	<0.01	0.01	0.05 mg/l
132/6-5-LE-KD-GC	-	0.02	-	-	0.02	-	-	-	<0.01	0.01	0.05 mg/l
132/6-6L-LE-KD-GC	-	-	-		-	-	-	-	-	-	0 mg/l
132/6-6S-LE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 mg/kg
132/6-7L-LE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 mg/l
132/6-7S-LE-KD-GC	-	-	4.7	1.9	-	-	-	-	-	-	6.6 mg/kg
134-IN-CD-LE-KD-GC	-	-	-	-	-		-	-	-	-	0 μg/m³
134-OUT-CD-LE-KD-GC	-	-	-	-	-	-	1.6	-	-	-	1.6 μg/m³
134-IN-PR-O-KD-GC	-	9	-	5.1	11.3	-	-	-	-	-	26 μg/m³
134-OUT-PR-O-KD-GC	-	86	12.9	17.5	14.5	-	-	-	0.8	7.1	139 μg/m³
134-IN-MR-O-KD-GC	-	318	-	-	-	-	-	-	-	-	318 μg/m³
134-OUT-MR-O-KD-GC	-	16.7	9.6	-	-	-	-	-	-	-	26.3 μg/m³
134-IN-CYR-O-KD-GC	-	90	10.6	250	214	9.0	7.4	0.3	18.6	26.0	626 μg/m³
134-IN-XR-SE-KD-GC	-	14.2	2.4	6.7	77.3	61.9	-	2.1	8.5	16.0	189 μg/m³
134-OUT-XR-SE-KD-GC	-	1.7	-	1.5	-	11.7	-	-	-	-	14.9 μg/m³
134-IN-1C-SE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-3C-SE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-10C-SE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-IN-PF-SE-KD-GC	-	-	-	-	-	-	-	-	-	-	0 μg/m³
134-OUT-PF-SE-KD-GC	-	128	17.8	-	-	-	-	-	-	-	146 μg/m³
133-18-SE-KD-GC	-	33.0	28.8	-	-	-	-	-	-	24.4	86.2 mg/kg

TABLE B-6. SAMPLE CODE FOR ORGANIC SAMPLES ANALYZED

SAMPLE CODE

XXXXX - XX - XX - XX - XX - X

Site Identification	Sample Type	Sample Preparation	First Level Analysis		Second Level Analysis	Third Level Analysis
132-IN, each test at inlet to scrubber 133-IN 134-IN 135-IN 136-IN 132-OUT, each test at scrubber outlet 133-OUT 134-OUT 135-OUT 136-OUT 132/6 represents composites of all samples taken	1 - boiler feedwater 2 - inlet to demisters 3 - settling pond overflow 4 - scrubber water inlet 5 - water to slag pond 6L - scrubber makeup liquid 7L - scrubber out liquid 6S - scrubber makeup solids 7S - scrubber out solids CD - condensate from XAD-2 module PR - solvent probe rinse C4R - cyclone rinse MR - solvent XAD-2 module rinse HM - HNO_3 XAD-2 module rinse HI - H2O2 impinger AI - APS impingers XR - XAD-2 resin PF - filter(s) 1C - 1-3μ cyclone 3C - 3-10μ cyclone 10C - >10μ cyclone CF - solid fuel feed (coal)	Number and corresponding preparation steps are as follows: 0 - no preparation LEA - liquid-liquid extraction, acified sample SE - solvent extraction A - acidified aliquot B - basic aliquot PB - Parr bomb combustion HW - hot water extraction AR - aqua regia extraction LEN - liquid-liquid extraction, neutralized sample LEB - liquid-liquid extraction, basified sample	Numbers and corresponding procedures are as follows:		Organic analyses on conc samples will be coded as follows: GM-GC/MS for PAHs GI-Grav., IR MS-LRMS LC-LC separation	Resulting LC fractions for grav./IR/LRMS analyses will be numbered in order, 1-8
			Organic	Inorganic		
			0-no conc require GC-C_7-C_{17} KD-K-D Cor	SS-SSMS AAS-Hg,As,Sb SO_4-SO4 NO_3-NO_3 CF-Cl,F		

TABLE B-6 (Continued)

Water Samples:		
132/6-1-LEA	132/6-1-LEN	132/6-1-LEB
132/6-2-LEA	132/6-2-LEN	132/6-2-LEB
132/6-3-LEA	132/6-3-LEN	132/6-3-LEB
132/6-4-LEA	132/6-4-LEN	132/6-4-LEB
132/6-5-LEA	132/6-5-LEN	132/6-5-LEB
Slurry Samples:		
132/6-6L-LEA	132/6-6L-LEN	132/6-6L-LEB
132/6-6S-LE	132/6-7L-LEN	132/6-7L-LEB
132/6-7L-LEA		
132/6-7S-LE		
SASS Train Samples:		
134-IN-PR		
134-OUT-PR		
134-IN-1C-SE		
134-IN-3C-SE		
134-IN-10C-SE		
134-IN-CYR		
134-IN-PF-SE		
134-OUT-PF-SE		
134-IN-XR-SE		
134-OUT-XR-SE		
134-IN-MR		
134-OUT-MR		
134-IN-CD-LEA	134-IN-CD-LEN	134-IN-CD-LEB
134-OUT-CD-LEA	134-OUT-CD-LEN	134-OUT-CD-LEB
Blanks		
H_2O Blank-LEA	H_2O Blank-LEN	H_2O Blank-LEB
133-MCB		
133-MAB		
133-XRB-SE		
133-PFB-SE		
CDB		

TABLE B-7. GRAVIMETRY OF SAMPLE CONCENTRATES

Sample	Weight mg/mℓ	Corrected for Blank mg/mℓ	Aliquot Factor	Sample Volume	Net Gravimetry
132/6-1-LE-KD-GI	0.4	0.4	X10	10ℓ	0.4 mg/ℓ
132/6-2-LE-KD-GI	0	0	X10	10ℓ	0
132/6-3-LE-KD-GI	0.5	0.5	X10	10ℓ	0.5 mg/ℓ
132/6-4-LE-KD-GI	0.3	0.3	X10	10ℓ	0.3 mg/ℓ
132/6-5-LE-KD-GI	0	0	X10	10ℓ	0
132/6-6L-LE-KD-GI	0.2	0.2	X10	8.5ℓ	0.2 mg/ℓ
132/6-6S-SE-KD-GI	0.2	0.1	X10	10.2g	98.0 mg/kg
132/6-7L-LE-KD-GI	0.1	0.1	X10	8.1ℓ	0.1 mg/ℓ
132/6-7S-SE-KD-GI	0.1	0	X10	10.6g	0
133-18-SE-KD-GI	0	0	X10	6.2g	0
134-IN-CD-LE-KD-GI	0.4	0.3	X10	31.1m^3	96.5 μg/m^3
134-OUT-CD-LE-KD-GI	0.4	0.4	X10	36.5m^3	109.6 μg/m^3
134-IN-PR-O-KD-GI	0.9	0.9	X10	31.1m^3	289 μg/m^3
134-OUT-PR-O-KD-GI	0.1	0.1	X10	36.5m^3	27.4 μg/m^3
134-IN-MR-O-KD-GI	0.9	0.9	X10	31.1m^3	289 μg/m^3
134-OUT-MR-O-KD-GI	0.8	0.8	X10	36.5m^3	219 μg/m^3
134-IN-CYR-KD-GI	7.5	7.5	X10	31.1m^3	2412 μg/m^3
134-IN-1C-SE-KD-GI	0	0	X10	31.1m^3	0
134-IN-3C-SE-KD-GI	0	0	X10	31.1m^3	0
134-IN-10C-SE-KD-GI	0	0	X10	31.1m^3	0
134-IN-PF-SE-KD-GI	0	0	X10	31.1m^3	0
134-OUT-PF-SE-KD-GI	0.52	0.26	X10	36.5m^3	71.2 μg/m^3
134-IN-XR-SE-KD-GI	1.89	1.45	X10	31.1m^3	446 μg/m^3
134-OUT-XR-SE-KD-GI	3.65	3.17	X10	36.5m^3	868 μg/m^3
133-XRB-SE-KD-GI	0.47				
133-MCB-O-KD-GI	0.1				
133-MAB-O-KD-GI	0				
133-CDB-LE-KD-GI	0.3				
132/6-LEB-LE-KD-GI	0				

TABLE B-8. INTERPRETATION OF INFRARED SPECTRA OF SAMPLE CONCENTRATES

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-IN-XR-SE-KD-GI	3280	W	OH or NH or C=0 overtone
	2920	S	C-H stretch
	1695	S	C=0
	1600	W	aromatics
	1450	M	-CH_2
	1365	W	-$C(CH_3)_x$
	1320	W	S=0 antisym stretch
	1270	S	C-0-C stretch
	1170	W	S=0 sym stretch
	1130-1050	M	ester and ether
	925	W	unassigned
	855	W	aromatics
	795	W	
	750	W	
	700	M	
			Indicates: esters, aldehydes/ketones, ether, sulfone - significant amount of aromatic species
134-OUT-XR-SE-KD-GI	2910	M	C-H stretch
	2650	W	acid
	2560	W	acid
	1680	S	C=0
	1600,1580	W	aromatics
	1450	W	CH_2
	1420	M	acid

TABLE B-8 (Continued)

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-OUT-XR-SE-KD-GI (con't.)	1320	M	sulfone S-O antisym stretch
	1285	S	C-O-C stretch
	1175	W	sulfone, S=O sym. stretch
	1130-1055	W	ester and ether
	1020	W	unassigned
	925	M	acid
	800	W	aromatics
	705	M	
	680	W	
	660	W	
			indicates: esters, carboxylic acids, ether & sulfone (reasonable amount of aromatic species)
134-IN-CYR-KD-GI	3400	M	OH, NH
	2920	S	C-H stretch
	1745-1650	S	C=O
	1600	W	aromatics
	1510	W	benzene rings or nitro compound
	1455	M	-CH$_2$
	1390-1355	M	-C(CH$_3$)x & nitro compound
	1270-1010	S	not sufficiently resolved
	1235	S	ester, acid sulfate or C-O-C in ring
	1170	M	ester, sulfate, phenol
	1110	M	alchol

TABLE B-8 (Continued)

Sample Identification	Band Location cm-1	Band Intensity	Compound Classification
134-IN-CYR-KD-GI (Con't).	1030	M	S=0 sulfoxide
	830	W	1,4-disubst benezene
134-OUT-PF-SE-KD-GI	2910	S	C-H stretch
	1740-1675	M	C=0
	1640,1630	W	C=C (mono or disubst.)
	1605	W	aromatic
	1505	S	aromatic nitro compound (or benzene ring)
	1460	M	$-CH_2$
	1410	W	carboxylic acid
	1385-1360	W	$-C(CH_3)x$
	1290	W	C-0-C stretch
	1235	S	C-0-C stretch for ester or alkyl acid sulfate or C-0-C in ring
	1180	S	C-0-C stretch for ester, sulfate or C-0-C in ring
	1135-1090	M	ether
	1035	M	S=0 stretch, sulfoxide
	825	M	1,4 disubst. benzene
			Indicates: esters, aldehydes/ketones, carboxylic acid, ether, covalent sulfate, alkyl acid sulfate, sulfoxide, possible nitro compound/significant aromatic character

TABLE B-8 (Continued)

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-IN-MR-KD-GI	2920	W	C-H stretch
			no identifiable species
134-OUT-MR-KD-GI	2920	S	C-H stretch
	1725	S	C=O
	1650	W	C-C (mono or disubst.)
	1450	M	$-CH_2$
	1290-1210	M	C-O-C stretch
	1120-1060	W	ester or ether
			Indicates: ester, possible ether
134-IN-PR-KD-GI	2920	S	C-H stretch
	1690	S	C-O
	1730	M	C=O
	1505	W	benzene ring or nitro compound
	1460	W	$-CH_2$
	1290	W	unassigned
	1230	M	C-O-C stretch
	1180	W	unassigned
			Indicates: unsaturated aldehyde or ketone & ester

Liquid Chromatographic (LC) Separations and Subsequent Analyses--

Liquid chromatographic separations are performed on only those samples having an organic content in excess of 500 μg/m^3 as determined by the gravimetric and TCO analyses. Whenever more than 10 percent of the total organic content is observed in the chromatographable portion, i.e., volatile materials represent a significant portion of the sample, special precautions are taken in preparing the sample for fractionation, and additional GC-TCO analyses are performed on the resultant samples. Using this criterion, a liquid chromatographic fractionation was needed and performed on samples 134-IN-XR-SE-KD, 134-OUT-XR-SE-KD and 134-IN-CYR-O-KD. In order to preserve volatile organics, all samples were introduced onto the LC column using the solvent exchange procedure described in Reference B-2. The seven fractions collected from the XAD-2 resin sample were analyzed for TCO just as were the original samples. The results of these C_7-C_{16} analyses are presented in Table B-9. All fractions were then evaporated to dryness in tared aluminum dishes. After the residues were weighed, an infrared analysis was done on all having a weight greater than 0.5 mg. The procedures followed were the same as used on the original samples. The gravimetric results for nonvolatile materials are shown in Table B-10. Table B-11 summarizes the classes of compounds identified in the infrared spectra produced by the residues.

Low Resolution Mass Spectroscopy (LRMS)--

Only fraction 5 of sample 134-OUT-XR contained enough material to require LRMS. Phthalates, benzoic acid, and aromatics, including the possibility of a nitro compound were reported as present.

Level 2 Data

Introduction--

With a few exceptions discussed below, the samples were prepared and extracted according to the procedures for Level 2 comparative assessment. These procedures are discussed elsewhere (Reference B-1). Details of special handling which is different from the Level 2 procedures are discussed in the following subsections. Compound identifications were made on the basis of the computerized mass spectral search of the 25,000 plus compounds in the

TABLE B-9. TCOs OF LIQUID CHROMATOGRAPHY FRACTIONS

	Hydrocarbons in Fraction, µg											
	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	Total	Amount Applied to Column
134-IN-XR-LC1	ND	ND	ND	25	158	292	125	ND	ND	88	688	
LC2	ND	ND	ND	35	ND	20	ND	20	149	182	406	
LC3	ND	ND	ND	37	ND	23	ND	21	ND	11	92	
LC4	ND	ND	61	ND	34	65	ND	ND	ND	ND	160	
LC5	29	380	ND	ND	20	35	126	34	ND	31	655	
LC6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	
LC7	LB	37	43	88	ND	ND	ND	ND	ND	ND	168	
											2169	3730
134-IN-CYR-LC1	ND	ND	ND	ND	ND	ND	ND	ND	24	51	75	
LC2	ND	ND	ND	ND	ND	ND	ND	ND	ND	18	18	
LC3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
LC4	ND	127	ND	ND	220	ND	ND	ND	ND	ND	347	
LC5	LB	453	ND	1065	43	19	ND	ND	39	20	1639	
LC6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
LC7	LB	15	60	ND	ND	ND	ND	ND	ND	ND	75	
											2154	52742
134-OUT-XR-LC1	ND	ND	ND	10	ND	ND	ND	ND	ND	ND	10	
LC2	ND	ND	ND	10	ND	ND	ND	9	16	ND	35	
LC3	ND	ND	ND	ND	ND	ND	ND	ND	ND	50	50	
LC4	ND	ND	ND	ND	49	108	29	ND	ND	ND	186	
LC5	ND	330	ND	ND	20	34	132	26	ND	19	561	
LC6	16	ND	ND	ND	ND	ND	ND	ND	ND	ND	16	
LC7	ND	40	ND	ND	ND	ND	ND	ND	ND	ND	40	
											898	1085

TABLE B-10. GRAVIMETRY OF LC FRACTIONS

	134-IN-XR	134-IN-CYR	134-OUT-XR
GRAV. of Material Applied to Column	9.45 mg	15.00 mg	18.25 mg
LC1	1.60	0.14	0.29
LC2	0.56	0	0.05
LC3	0.33	0	0.15
LC4	0.43	0.09	0.32
LC5	3.18	3.22	10.79
LC6	2.41	2.78	3.80
LC7	0.99	1.49	1.01
Total	9.50	7.72	16.41
Blank Correction	0.46	0.39	0.46
Net Gravimetry	9.04	7.33	15.95
	BLANK		
LC1	0.12 mg		
LC2	0.03		
LC3	0.04		
LC4	0.03		
LC5	0.04		
LC6	0.13		
LC7	0.07		
Total	0.46		

TABLE B-11. INTERPRETATION OF INFRARED SPECTRA OF LC FRACTIONS

Sample Identification	Band Location, cm^{-1}	Band Intensity	Compound Classification
134-IN-XR-LC1	3000-2800	S	Aliphatic HC
	1450	M	Aliphatic HC
	1380	W	Aliphatic HC Indicates: Aliphatic hydrocarbon
134-IN-XR-LC2	3020	M	Unsaturated or aromatic HC
	3000-2900	S	Aliphatic HC
	1600	M	Aromatic
	1490	M	
	1450	M	CH_2 (aliphatic)
	1110	M	
	1050	W	Unassigned
	1030	W	
	890		Aromatic substitution
	830		
	800		
	750		
	700		
			Indicates: Aliphatic & aromatic hydrocarbons
134-IN-XR-LC5	3300	S, broad	OH, NH
	3060	W	aromatic CH
	3000-2800	S	Aliphatic CH
	1710	S, broad	C=O ester, ketone
	1610	M	aromatic
	1590	W	aromatic
	1460	S	methyl
	1420	W	methyl
	1370	W	methyl

TABLE B-11 (Continued)

Sample Identification	Band Location cm-1	Band Intensity	Compound Classification
	1270	S, broad	C-O of benzoate esters
	1180	W	
	1120	W	C-O
	1070	W	
	1030	W	aromatic substitution
	810	W	
	760	W	
	720	S	
			Indicates: aliphatic & aromatic hydrocarbons, alcohols, esters, ketones
134-IN-XR-LC6	3350	M	OH, NH
	3050	W	unsaturated or aromatic CH
	3000-2800	S	aliphatic CH
	1700	S, broad	C=O - acid, aryl/unsaturated ester or ketone
	1600	S	aromatic ring, skeletal or amine
	1550	S	COO^-
	1450	M	aliphatic CH_2
	1400	S	COO^-, alkenes
	1320	W	sulfone
	1260	M	C-O, ester, carboxylic acid

TABLE B-11 (Continued)

Sample Identification	Band Location, cm^{-1}	Band Intensity	Compound Classification
	1170	W	sulfone, ether
	1120	M	C-O, alcohol
	715	M	aromatic subst.
			Indicates: aromatic & aliphatic species: aryl or unsaturated ester, ketone, nitro compound, carboxylate, carboxylic acid; possible amine, alcohol
134-IN-XR-LC7	3000-2800	S	aliphatic CH
	1730	M	C=O, broad, ester
	1550	M, broad	COO^-
	1400	M, broad	COO^-
	1270	M, broad	C-O, ester
			Indicates: aliphatic ester, carboxylic acid salt
134-OUT-XR-LC-5	3200-2500	S, broad	acid OH
	1690 (1720-1680)	S, broad	C=O, ester, ketone, acid
	1600	M	aromatic ring
	1580	M	
	1490	W	unassigned
	1450	M	$-CH_2$
	1420	M	C-O, acid
	1320	M	C-O, acid, sulfone
	1290	S	C-O of acid, phthalate ester
	1180	M	sulfone
	1120	M	C-O of ester, possibly phthalate
	1070		
	1020		

TABLE B-11 (Continued)

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-OUT-XR-LC-5	920		aromatic substitution
	800		
	710		
			Indicates: carboxylic acids, ester & nitro aromatic
134-OUT-XR-LC6	3350	S, broad	OH, NH
	3050	W	aromatic CH
	3000-2800	S	aliphatic CH
	1670 (1645-1720)	W, broad	C=C or amide (C=O buried?)
	1600	S	aromatic
	1540		-COO$^-$; amide
	1450	W	-CH$_2$
	1400	S	-COO$^-$
	1260 (1230-1280)	S, broad	C-O of aromatic ester, acid, alcohol
	1170	W	phenol
	1060	M	C-N of amine
	710	S	aromatic subst.
			Indicates: aliphatic & aromatic esters, alcohol, carboxylic acid, carboxylate, nitro compound, possible amine
134-OUT-XR-LC7	3300	M	OH, NH
	3050	W	aromatic C-H
	3000-2800	S	aliphatic C-H
	1720	S	C=O - ester, ketone
	1600	S	aromatic ring

TABLE B-11 (Continued)

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-OUT-XR-LC7 (Con't)	1550	S	COO$^-$, or nitro compound
	1450	M	-CH$_2$
	1400	S	COO$^-$
	1370	M	CH$_2$, nitro compound
	1270	S	C-O-C stretch, ester
	1100	M	C-O, alcohol, ester, ether
	710	M	aromatic substitution
			Indicates: aliphatic & aromatic ester, alcohol, possible carboxylate, nitro compound, ether
134-IN-CYR-LC5	3400	S	OH, NH
	3050	W	aromatic CH
	3000-2800	S	aliphatic CH
	1700 (1650-1720)	S, broad	-C=O, unsaturated ester, ketone acid possible amine
	1450	S	aliphatic HC
	1370	S	possible sulfonate
	1260	S, very broad	C-O, ester, ether, acid, alcohol possible sulfonate, amine
	1180	W	
	1130	W	
	730	W	unassigned
	710	W	
			Indicates: ester, ketone ether, acid alcohol some unsaturation, possible phenols, sulfonate

TABLE B-11 (Continued)

Sample Identification	Band Location cm^{-1}	Band Intensity	Compound Classification
134-IN-CYR-LC6	3300	M	OH or NH
	3050	W	unsaturated CH
	3000-2800	S	aliphatic CH_2
	1720	S	C=O ester, ketone
	1610	S	C=C, amine
	1465	M	CH_2
	1375	W	dimethyl, possible sulfonate
	1150 (1050-1300)	M	C-O, alcohol ether, ester, amine N-H stretch
			possible sulfonate
			Indicates: aliphatic ester, ketone, alcohol, ether; possible phenol, sulfonate.
134-IN-CYR-LC7	3000-2800	W	aliphatic CH
	1700	W	C=O
	1110	W	
			no identifiable activity

National Bureau of Standards compound library. Acceptance of the search results involves judgemental factors. Some incorrect identifications may, therefore, exist in the tables. A final confirmation by GC relative retention time and spectral comparison with known standards was not performed. However, not all samples were subjected to quantitation or confirmation because the initial screening showed very low concentration levels and budget and schedule considerations limited further efforts.

Several representative samples from the various sample groups e.g., probe rinses, resin extracts, condensates, etc. have undergone a procedure to estimate compound concentrations. Each representative sample was selected on the basis of the greatest number of compounds detected and the highest apparent levels. The remaining samples have fewer detected compounds and/or lower levels. The next step was to identify potentially hazardous compounds which exceed minimum established levels (Figure B-3, Logic Flow Chart for Level 2 Organic Analysis and Figure B-3, Analysis of Samples from Sampling Train). The process water extracts have been analyzed to the point prior to concentrations for LC fractionation (see Figure B-4).

Estimation of Concentration Levels--

The following is a summary of the procedure by which compound concentrations in selected samples were estimated for comparison with DMEG values. An internal standard solution of naphthalene and chloronapthalene was prepared in methylene chloride at 10 μg/ml for each standard. One hundred μl of this solution was blended with one hundred μl of a sample to be reanalyzed by GC/MS for quantitative purposes. The result was a solution containing the internal standards at 5 μg/ml and the original sample solution at one half of its original concentration. This solution was analyzed by GC/MS using the same conditions as with the original screening analysis. A total ion chromatogram was obtained and the areas for all chromatogram peaks of interest were obtained. One of the compounds in the sample was selected as a secondary standard and its concentration estimated on the basis of the known concentration of the internal standard and the ratio of the peak areas of the secondary standard and the internal standard. Then, having an estimated concentration of the compound used as a secondary standard, the data from the original screening analysis was used to obtain

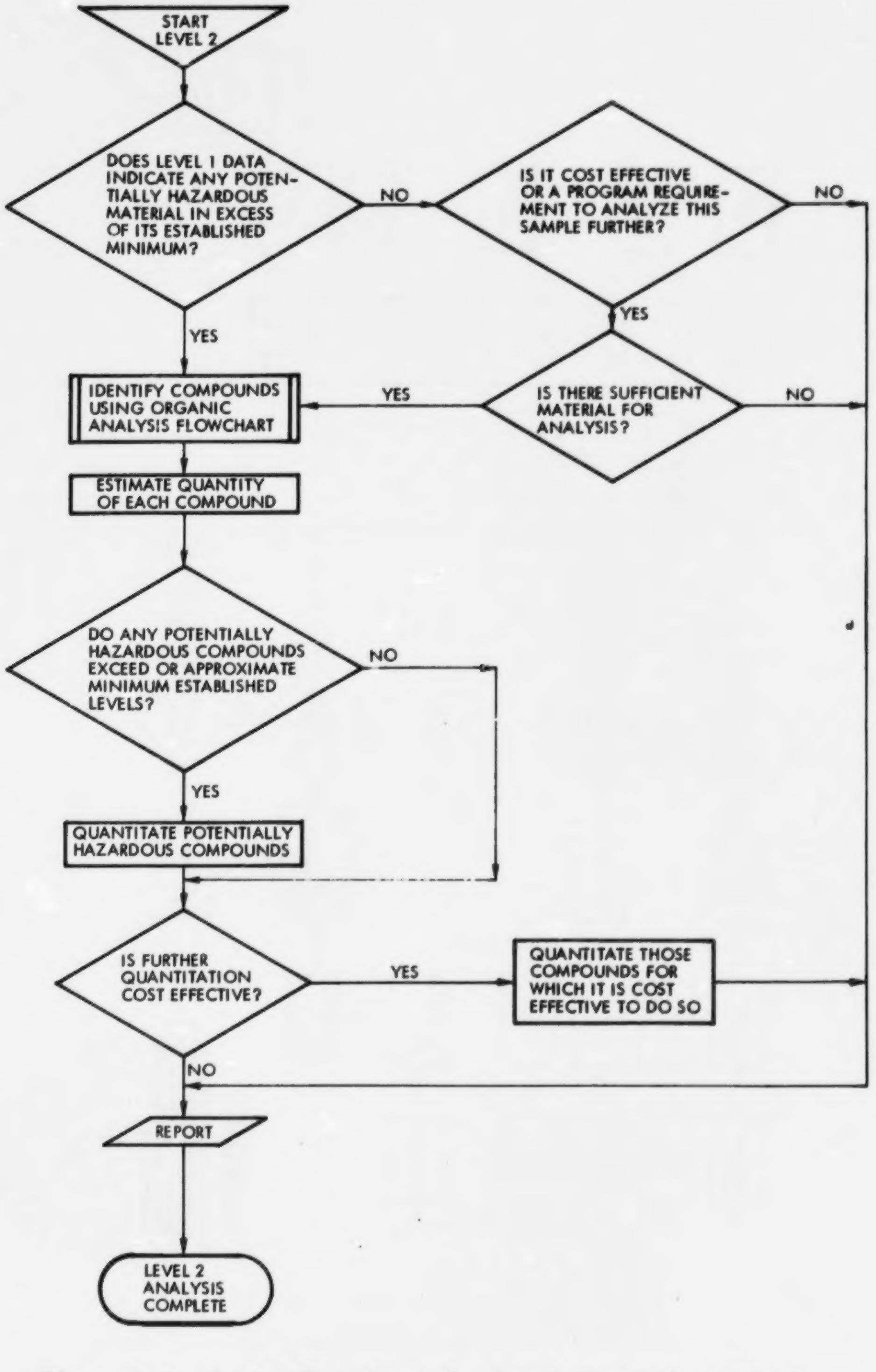
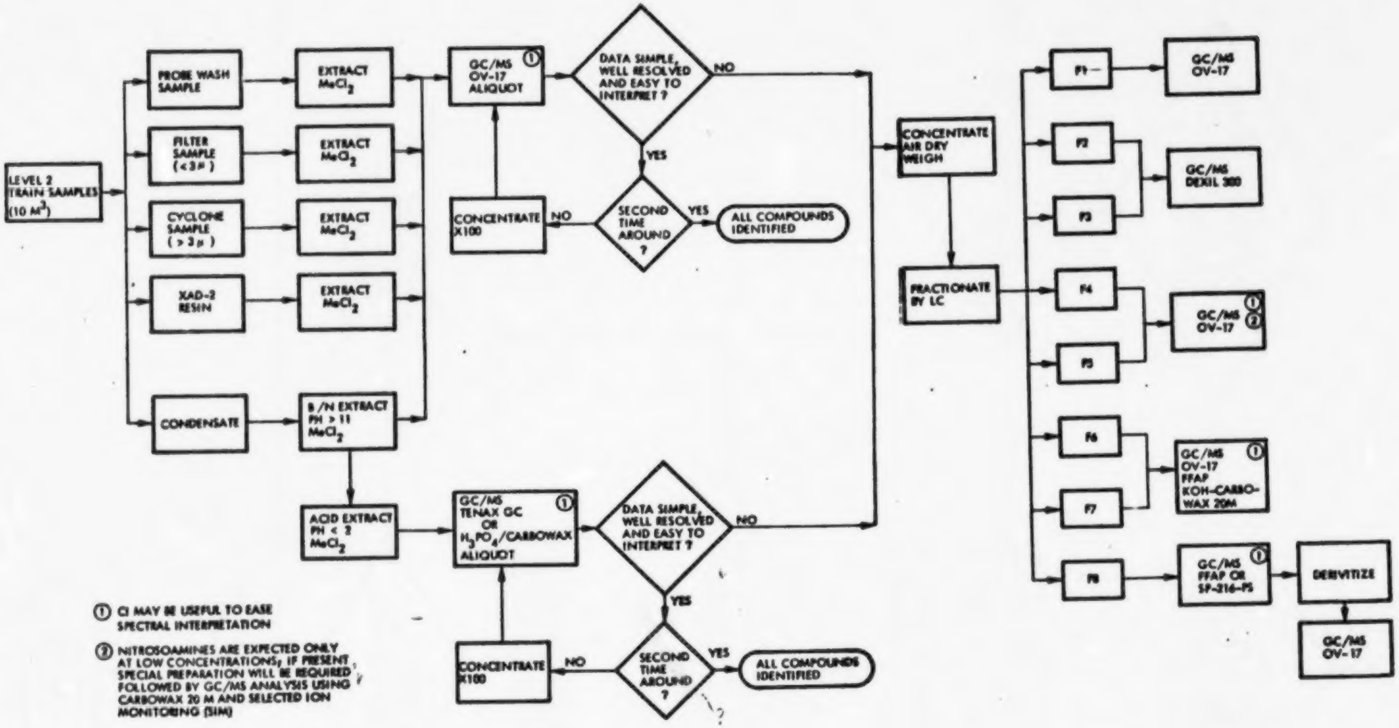

START LEVEL 2
DOES LEVEL 1 DATA INDICATE ANY POTENTIALLY HAZARDOUS MATERIAL IN EXCESS OF ITS ESTABLISHED MINIMUM?
NO
IS IT COST EFFECTIVE OR A PROGRAM REQUIREMENT TO ANALYZE THIS SAMPLE FURTHER?
NO
YES
YES
IDENTIFY COMPOUNDS USING ORGANIC ANALYSIS FLOWCHART
YES
IS THERE SUFFICIENT MATERIAL FOR ANALYSIS?
NO
ESTIMATE QUANTITY OF EACH COMPOUND
DO ANY POTENTIALLY HAZARDOUS COMPOUNDS EXCEED OR APPROXIMATE MINIMUM ESTABLISHED LEVELS?
NO
YES
QUANTITATE POTENTIALLY HAZARDOUS COMPOUNDS
IS FURTHER QUANTITATION COST EFFECTIVE?
YES
QUANTITATE THOSE COMPOUNDS FOR WHICH IT IS COST EFFECTIVE TO DO SO
NO
REPORT
LEVEL 2 ANALYSIS COMPLETE

Figure B-3. Logic flow chart for Level 2 organic analysis


LEVEL 2 TRAIN SAMPLES (10 M^3)
PROBE WASH SAMPLE
FILTER SAMPLE (< 3 μ)
CYCLONE SAMPLE (> 3 μ)
XAD-2 RESIN
CONDENSATE
EXTRACT $MeCl_2$
EXTRACT $MeCl_2$
EXTRACT $MeCl_2$
EXTRACT $MeCl_2$
B/N EXTRACT PH > 11 $MeCl_2$
ACID EXTRACT PH < 2 $MeCl_2$
GC/MS OV-17 ALIQUOT ①
GC/MS TENAX GC OR H_3PO_4/CARBOWAX ALIQUOT ①
DATA SIMPLE, WELL RESOLVED AND EASY TO INTERPRET ?
NO
YES
SECOND TIME AROUND ?
YES
NO
ALL COMPOUNDS IDENTIFIED
CONCENTRATE X100
DATA SIMPLE, WELL RESOLVED AND EASY TO INTERPRET ?
NO
YES
SECOND TIME AROUND ?
YES
NO
ALL COMPOUNDS IDENTIFIED
CONCENTRATE X100
CONCENTRATE AIR DRY WEIGH
FRACTIONATE BY LC
F1
F2
F3
F4
F5
F6
F7
F8
GC/MS OV-17
GC/MS DEXIL 300
GC/MS OV-17 ① ②
GC/MS OV-17 FFAP KOH-CARBO-WAX 20M ①
GC/MS FFAP OR SP-216-PS ①
DERIVITIZE
GC/MS OV-17

① CI MAY BE USEFUL TO EASE SPECTRAL INTERPRETATION

② NITROSOAMINES ARE EXPECTED ONLY AT LOW CONCENTRATIONS; IF PRESENT, SPECIAL PREPARATION WILL BE REQUIRED FOLLOWED BY GC/MS ANALYSIS USING CARBOWAX 20 M AND SELECTED ION MONITORING (SIM)

Figure B-4. Analysis of samples for organic content peak areas for all compounds of interest. Concentration estimates were obtained for all significant compounds on the basis of peak areas relative to the secondary standard. Using total ion chromatogram peak areas for different types of compounds is only useful for estimates because of several variable factors affecting the recorded ion output per unit amount of any group of compounds. The levels presented in the tables are believed to be accurate to plus or minus a factor of 10. Should the need arise for more accurate concentrations for any given compound, then special mixtures containing known amounts of internal standard and the compounds of interest will have to be prepared and run on the GC/MS to determine relative response factors. These relative response factors can then be applied to the original sample data. Alternatively the original samples solutions can be spiked with known added amounts of specific compounds and reanalyzed. This generally is called the method of standard additions.

GC/MS Analysis of Gas Bag Samples--

Handling of these samples proceeded as follows. Two liters of gas bag sample was passed through a pre-conditioned Tenax column. The Tenax column was then heated and the absorbed species transferred to a liquid nitrogen cooled trap. The LN_2 trap was then allowed to come to room temperature while isolated from the system with closed valves. The contents of the trap were then injected onto a GC column. The GC separation was accomplished using the following conditions:

Column - 6 ft stainless steel containing Poparak Q 60-80 mesh

Carrier - Helium at 30 cc per minute

Temperature - Programmed from $50^{\circ}C$ to $230^{\circ}C$ at $8^{\circ}C$ per minute and held at 230°C for 15 to 30 minutes

The mass spectrometer was used as the GC detector in a mode which scanned the mass range in continuous cyclic recordings. Quantification of the compounds was performed using peak areas. Determination of instrument response to the detected compounds (i.e., calibration) was done directly using a synthetic gas blend.

A summary of the organic compounds found in the gas bag samples and their calculations is presented in Table B-12. Units of concentration are expressed in milligrams per cubic meter of gas sample at 1 atmosphere and 21°C.

The results generally indicate that the levels found in the samples do not significantly exceed the levels found in the blank. The background levels for these compounds in the blank sample appear to be rather high.

There are scattered instances where six compounds have consistently higher concentrations than those found in the blank sample. The six compounds are methyl methacrylate, a C_7 hydrocarbon, an additional hydrocarbon of similar but not accurately known molecular weight, trichloroethylene, methylisobutyl ketone, and xylene. It is believed that these higher levels result from variation in blank levels but this cannot be statistically confirmed because several blanks would be required to determine a range of variation and these multiple blanks were not obtained.

GC/MS Analysis of SASS Train Sample Catches--

This section presents the results of the GC/MS analysis on the extracts and rinses taken from the SASS train components. These samples are reported in the following groups:

- Probe rinses, cyclone catch extracts, particulate filter extracts, and cyclone rinses.
- Sorbent resin extracts.
- Resin module rinses and condensate extracts.

These groupings were made to report samples most likely to contain similar compounds.

Analysis of Probe Rinse, Particulate Catch and Cyclone Rinse Samples--

This section describes the results of the analysis of the probe and cyclone rinses as well as the extracts from the particulate matter which was found in the cyclones and filters. These samples as a unit represent the organic compounds found in the train upstream of the resin module. No compounds of any significance were found in any of the unconcentrated extracts. The following discussion deals with the analysis of the samples

TABLE B-12. RESULTS OF GAS BAG ANALYSIS

Compound	Concentration, mg/m^3								
	132 (Blank)	132 In	132 Out	134 In	134 Out	135 In	135 Out	136 In	136 Out
Dichlorofluoromethane	0.13	0.13	0.39	0.04	0.26	0.08	0.85	0.30	0.08
Vinyl Chloride	0.05	0.05	0.08	0.02	0.13	0.05	0.18	0.08	0.08
Methyl Formate	0.18	0.15	0.25	0.15	0.28	0.20	0.18	0.07	0.25
Methylene Chloride	11.9	11.2	11.9	11.2	11.2	13.0	13.0	11.6	13.6
Diethyl Ether	5.9	5.5	5.9	7.0	5.1	7.0	6.3	5.9	7.0
Tetrahydrofuran	1.8	2.4	3.0	3.6	3.6	3.0	3.9	3.9	4.5
Unsaturated Hydrocarbon	1.2	0.4	1.2	1.7	1.7	1.7	0.4	1.7	2.1
Carbontetrachloride	12.7	5.1	5.7	8.2	10.8	7.0	11.4	7.6	12.7
Methyl Methacrylate	1	2	2	4	2	2	2	3	3
Hydrocarbon (C_7)	ND*	0.8	0.4	0.04	0.04	0.13	0.4	ND*	0.4
Toluene	6.9	4.6	6.5	8.0	5.8	8.4	8.0	9.6	10.0
Hydrocarbon	0.17	0.33	ND*	0.83	ND*	ND*	ND*	ND*	ND*
Trichloroethylene	ND*	4.	5.	4.	ND*	4.	ND*	4.	ND*
Methylisobutylketone	ND*	0.3	0.3	2.5	0.4	1.7	1.2	ND*	1.2
Xylene	ND*	ND*	ND*	ND*	ND*	3.5	ND*	0.4	4.4

* ND = Not detected — limit of detection is 0.02 mg/$_m$3.

which were concentrated by sample evaporation. Separation by liquid chromatography was not necessary. Identified compounds are summarized in Table B-13. Estimated concentrations are presented for the major components.

Both probe rinse samples contain large quantities of 3-methylene-2-pentanone. This is an acetone condensation product. The acetone is part of the rinse solvent and it is likely that this compound has its origin in the rinse solvent. The probe rinse from the SASS train at the scrubber inlet contained only the diacetone condensation product at significant levels. The concentrated probe rinse from the sample train at the scrubber outlet contained additional compounds. Table B-13 shows additional ketones, a possible C_6 tertiary amine and a naphthalene substituted silane. The concentrated extracts from the particulate material caught in the cyclones and on the filter of the scrubber inlet sample train contained very little organic material. A freon, either $C_4Cl_4F_6$ or $C_4Cl_3F_7$ was common to all these samples. The 1 micron cyclone catch had three peaks which could not be confidently identified using the computerized library search. They currently remain unknown and are not believed to be present at levels greater than the other reported species.

The combined cyclone rinse concentrate was found to contain an extensive number of compounds as shown in Table B-14. Ketones, substituted naphthalenes and benzenes predominated. Several small condensed aromatics were also believed to be present. These include acridine, and a possible acenaphthalene. Concentration levels for the compounds found in the cyclone rinse were estimated using total ion GC peak areas.

The estimated concentrations of compounds found in the cyclone rinse were compared to the appropriate DMEG values as shown in Table B-14. In most cases, compounds in the sample could not be found in the DMEG charts; in those cases, the DMEG value for the most similar compound listed was used. All DMEG values were at least 1000 times larger than the concentrations of corresponding compounds found in the cyclone rinse.

Sorbent Resin Extracts--The compounds which were extracted from the sorbent resin and are believed to have been present in the sample effluent gas are presented in Table B-15. The concentrated extracts were analyzed

TABLE B-13. PROBE RINSES, PARTICULATE EXTRACTS, CYCLONE RINSES

	134 Scrubber Inlet			134 Scrubber Outlet		
Sample	Compound	Extract Concentration µg/ml	Gas Concentration µg/m^3	Compound	Extract Concentration µg/ml	Gas Concentration µg/m^3
Probe rinse	3-Methylene-2-pentanone			3-Methylene-2-pentanone		
				3-Methylene-3-pentanone		
				Possible N,N-Dimethyl butanamine		
				2-Methyl-2-octen-4-one		
				2,5-Dimethyl-2,5-hepadiene-4-one		
				Trimethylnaphthalenyl Silane		
1 Micron Cyclone Catch Extract	Freon, $C_4Cl_3F_7$ or $C_4Cl_4F_6$	2	0.6	No cyclones used on scrubber outlet SASS train.		
	Unknown, apparent molec. wt. 529	4	1			
	Unknown, apparent molec. wt. 470	7	2			
3 Micron Cyclone	Freon, [$C_4Cl_3F_7$ or $C_4Cl_4F_6$] O-Methyl-benzalde-oxime			No cyclones used on scrubber outlet SASS train.		
10 Micron Cyclone Catch Extract	3-Methylene-2-pentanone Unknown.			No cyclones used on scrubber outlet SASS train.		
Particulate Filter Extract	Freon, $C_4Cl_3F_7$ or $C_4Cl_4F_6$			Freon, [$C_4Cl_3F_7$ or $C_4Cl_4F_6$] MW 154: Dihydroacenaphthalene or Biphenyl.		

TABLE B-14. ANALYSIS OF CYCLONE RINSE TEST 134, SCRUBBER INLET SAMPLING TRAIN

Compound	Concentration In Extract µg/ml	Emission Concentration In Gas Stream µg/m^3	Representative DMEG Value µg/m^3
3-Methylene-2-pentanone	4×10^2	1×10^2	2.5×10^4
Trimethylbenzene	2	0.6	1.2×10^5
2,6-Piperiden-dione-4,4-dimethyl	6×10^1	2×10^1	4×10^4
2,6-Dimethyl-2,5-heptadien-4-one	4×10^1	1×10^1	2.5×10^4
4(2-butenyl)-1,2-dimethylbenzene	1	0.3	2×10^5
Decahydronaphthalene	0.3	0.1	2×10^5
Phenyl (2,2,3-trimethyl cyclopentilidene methane)	5	2	6×10^4 1×10^6
Trimethylnaphthalenylsilane	4	1	5×10^4
5-Methyl-benz-c-acridine	0.7	0.2	5×10^4
2,6-bis (1,1-Dimethylethyl) naphthalene	0.9	0.3	2×10^5
Hexamethylhexahydroindacene	1	0.3	N
Long Chain Acid; Methyl ester (> C_{14})	0.6	0.2	N
Di Tert-butyl naphthalene	1	0.3	2×10^5
Dimethylisopropylnaphthalene	1	0.3	2×10^5
Hexamethylbiphenyl	2	0.6	1×10^3
Cyclohexylbenzene	0.8	0.3	2×10^5

N = No DMEG value given: either compound structure is unclear or no biological toxicity data is available in the literature.

TABLE B-15. ABSORBENT RESIN EXTRACTS

Compound	μg/ml	$\mu g/m^3$	DMEG Values ($\mu g/m^3$)
134 SCRUBBER INLET			
2,3-Dimethyldecahydronaphthalene	<0.1	<0.03	2×10^5
1,3-Diethylbenzene	7	2	4×10^5
C_6 substituted Benzene	3	1	2×10^4
1,2,3,4-Tetrahydronaphthalene	<0.1	<0.03	2×10^5
Dihydronaphthalene	1	0.03	1×10^5
1,3,5-Triethylbenzene	1	0.3	2×10^5
C_{10} substituted Naphthalene	0.2	0.06	2×10^5
C_{10} substituted Decahydronaphthalene	4	1	4×10^6
Ethylbenzaldehyde	11	4	6×10^4
Dimethylbenzaldehyde	2	0.6	6×10^4
Methylnaphthalene	4	1	4×10^6
Unknown: possible substituted Anthracene or Phenanthrene	1	0.3	2×10^4
Methylnaphthalene	2	0.6	4×10^6
1,1'-Biphenyl	12	4	1×10^3
9,10-Dihydrophenanthrene or 1-1'-Diphenylethene	0.6	0.2	4×10^5
Unknown - Apparent mole wt. 242	5	2	N
1,1-Bis (p-ethylphenyl)-ethane or Tetramethylbiphenyl. Three isomers present	25	8	1×10^3
Another Tetramethylbiphenyl	4	1	1×10^3
2-Phenylnaphthalene	1	0.3	1×10^3
134 SCRUBBER OUTLET			
C_3 substituted Benzene	1	0.3	2×10^4
Ethylbenzaldehyde	10	3	6×10^4
Tetramethylbenzene	<0.1	<0.03	2×10^5
2,4-Dimethylacetophenone	2	0.6	4×10^4
Trimethylcychexenone	4	1	6×10^6
Nitric acid decylester	1	0.3	N

N = No DMEG value given.

by GC/MS using an OV-17 column with a temperature program from 50°C to 280°C. (See Reference B-1 for details.)

Both extracts from the trains at the scrubber inlet and outlet had extensive amounts of the many compounds that were also extracted from the blank resin sample. The relative amounts of materials common to both samples and the blank vary somewhat between the two resin extract samples, and the following general observations can be made. Of the compounds common to the blank and the outlet resin samples, the amounts found in the outlet sample generally were 1/4 to 1/2 the amount found in the blank. Ten to 15 times greater amounts were found at the scrubber inlet than in the resin blank. All of these resins had been precleaned in the same lot, therefore, lot to lot variation is not suspect.

The cause of these variations is the resin cleaning specification. The program specifications for clean XAD-2 resin is as follows:

- Acceptable - TCO and Grav. < 5 mg/150 g
    - TCO < 1.5 mg/150 g
    - Grav. < 3.75 mg/150 g
- Marginal - TCO and Grav. 5-7 mg/150 g
- Unacceptable - TCO and Grav. > 7 mg/150 g

The SASS train resin module contains 150 g of resin. These specifications were developed at the beginning of the EACCS program, and they are compatible with the latest revision of the Level 1 manual. The total of TCO compounds found at the scrubber inlet (Table B-15) was 26.3 $\mu g/m^3$ or 789 μg in 30 m^3 or 789 μg in 150 g of resin. Similarly, the total of compounds found at the scrubber outlet (Table B-15) was 5.2 $\mu g/m^3$ or 156 μg in 30 m^3 or 156 μg in 150 g of resin. The TCO requirement for resin acceptability was < 50 $\mu g/m^3$ (1500 μg per 150 g) which was greater than the levels of compounds being sought. Thus, the blank ranged from 1.9 to 9.6 times greater than the levels being sampled.

This shows that resin cleaned for Level 1 is not suitable for Level 2 sampling and analysis. The problem described above will occur whenever Level 2 analyses are performed on resin samples acquired by Level 1 procedures.

A computerized data manipulation and compound search technique was used to increase the level of confidence in the reported compounds presented in Table B-15. The procedure was required because of the presence of resin artifact background interference. The blank resin extract data were searched for the presence of every compound found in the two sample resin extracts. The technique consisted of selecting a peak which was present in the inlet or outlet sample resin extracts. A mass spectrum was obtained for the peak and several characteristic masses specific to the compound were noted. The blank resin data was searched for a peak caused by the selected characteristic masses. If a peak occurred in the appropriate retention time window the entire mass spectrum was searched for compound identification. If the Library search results or the spectra were the same the compound was deemed to be a resin artifact. If no peak was observed in the blank resin chromatogram, the compound was deemed to be not from the resin but rather from the sample effluent gas. This selected mass search technique was performed for each peak where any doubt existed as to origin. The compounds which passed this test and are believed to originate in the sample effluent gas are the ones presented in Table B-15.

The compounds seen in the scrubber inlet resin extract generally consist of substituted benzenes, naphthalenes, and biphenyls. A few benzaldehydes were also found. A few possible condensed aromatics such as substituted phenanthrenes were tentatively identified but further confirmation would be required for certainty. The scrubber outlet resin extract contains substituted benzenes and ketones. It is important to note that one of the major classes of compounds extracted from the blank resin are also substituted benzenes, naphthalenes, and biphenyls. Thus, some of the reported substituted benzene compounds may still be artifacts, i.e., compounds remaining in the resin after pre-cleaning and blank extraction but which become extractable after being used in the sample train.

The resin extract samples from both the scrubber inlet and scrubber outlet sample trains were subjected to the concentration estimation procedures and these estimates were compared with DMEG values (Table B-15). In nearly all cases, the ratio of the DMEG values to the estimated concentrations in the LaCygne effluent exceeded 10,000 to 1. Exceptions were biphenyl and four compounds believed to be alkyl substituted biphenyls. The ratios of DMEG values to effluent gas concentration estimates for these exceptions ranged between 100 to 1 and 1000 to 1. These effluent compounds are believed to be present in the resin extracts at concentration levels much lower than those levels at which further analysis would be recommended.

Analysis of Resin Module Rinsings and Aqueous Condensate Extracts-- This section summarizes the results of the analysis on the module rinses and module condensates from the scrubber inlet and scrubber outlet sample trains. These two sample groups are discussed together as they are intended to contain materials which do not advance as far as the resin canister or which pass through the resin module without being trapped on the resin. The condensates were extracted after sequential pH adjustment to acidic, neutral and alkaline conditions. The module rinses in acetone/ methylene chloride required no such extraction. These extracts were analyzed in both concentrated and non-concentrated forms. The details of these procedures are presented in Reference B-1.

The unconcentrated extract solutions and rinses were analyzed to check for volatile species present in a sample effluent which could be lost as a result of evaporation during solvent removal. No volatile compounds were seen in the unconcentrated extracts or rinses at detectable levels other than solvent species. Instrument detection levels, calculated to reflect gaseous effluent concentration levels, are 0.03 $\mu g/m^3$.

The results of these module rinses and condensate analyses are summarized in Table B-16. The module rinse from the scrubber inlet train contained only a diacetone condensation product and one unknown. The diacetone is believed to be from the acetone/methylene chloride rinse solution. The module rinse from the scrubber outlet train has four carboxylic esters, a C_4 Freon and one C_6 ketone. This sample was reanalyzed by GC/MS with an internal standard to estimate concentration levels. The species were estimated to be present at gaseous effluent levels all below 1 $\mu g/m^3$.

The concentrated extract of the acidified condensate from the scrubber inlet train was found to contain no reportable levels of material. The

TABLE B-16. MODULE RINSES AND CONDENSATE EXTRACTS

Sample	134-Scrubber Inlet Compound	Concentration in sample µg/ml	Concentration in flue gas µg/m^3	Typical DMEG Value	134-Scrubber Outlet Compound	Concentration in sample µg/ml	Concentration in flue gas µg/m^3	Typical DMEG Value
Module Rinse	3-Methylene-2-pentanone Unknown	---------Not Quantitied----------			Butylacetate 1-(2-methyl) cyclopropylethanone Freon Methyl ester of carboxylic Acid (3 Separate Compounds)	1 0.3 0.4 1	0.3 0.1 0.1 0.3	1 x 10^5 6 x 10^6 N N
Acidified Condensate Extract; pH < 2	No Compounds Detected	---------Not Quantitied----------			5-Ethyl-2-methyl-t-heptene-3-one 1 Butanol-3-methylbenzoate	---------Not Quantified-----------		
Neutral Condensate Extract; pH 7	Possible Methylisopropylphenol Freon: $C_4Cl_3F_7$ or $C_4Cl_4F_6$ Possible 5,7-Dihydro-6H-dibenzo/A,C/cycloheptene-6-one	---------Not Quantitied----------			Possible 5,7-Dihydro-6H-dibenzo/A,C/cycloheptene-6-one	---------Not Quantified-----------		
Basic Condensate Extract; pH 11	No Compounds Detected	---------Not Quantified----------			Freon: $C_4Cl_3F_7$ or $C_4Cl_4F_6$ Possible 5,7-Dihydro-6H-dibenzo/A,C/cycloheptene-6-one	7 2	2 0.6	N 4 x 10^4

N = No DMEG value given: No biological toxicity data in literature.

lower limit of detection expressed in terms of concentration in a gaseous effluent is estimated to be 0.03 μg/m^3. The acidified condensate extract from the scrubber outlet train contained what is believed to be a branched C_{10} ketone and a butyl ester of methyl benzoate. No repeat analysis was made to quantify these compounds but inspection of the total ion chromatograph data indicated their presence at gaseous effluent levels of much less than 1 μg/m^3. The condensate extracts after adjustment to neutral and alkaline pH also showed very little material. Table B-16 shows one ketone, one phenyl substituted hydrocarbon, a Freon and a possible C_4 substituted phenol. The possible presence of the phenol in a neutral fraction is unexplained except for the possibility that the compound identification on the basis of mass spectral data is in error. No reanalysis of this sample was made to resolve this anomaly because of the apparently insignificant concentrations.

The basic condensate extract from Run 134 was rerun with an internal standard to estimate concentration levels of the two species that were identified. Table B-16 shows microgram and submicrogram per cubic meter levels. Again these levels are at least a factor of a thousand below typical DMEG values.

Process Water and Slurry Extracts--

This section summarizes the results of the GC/MS analyses on the process water and slurry extracts. Two GC column systems were used for effective separation of the acid species and the basic species as separate entities. Refer to Reference B-1 for procedural details. Additional chromatography, i.e., the OV-17 screening GC/MS was also employed to analyze the acidic fractions for neutral species as well as to provide backup data for reporting confidence in observed species. The order of presentation in Tables B-17 and B-18 is acidified extracts followed by the neutral and basic extracts.

The procedure used for the extraction of the aqueous samples such as the process waters, the slurries and the aqueous SASS train condensates

TABLE B-17. ACIDIFIED PROCESS WATER AND SLURRY SAMPLES

	132/6-1	132/6-2	132/6-3	132/6-4	132/6-5	132/6-6L	132/6-7L
4-Hydroxy-4-methyl-2-pentanone	X				X	X	
2,2,4-Trimethyl cyclohexene-1-methanol							
2-Ethyl hexanoic Acid							
2H-Pyran-2-one or 2-cyclohexene-1-one	X			X			
4-Chloro-trans cyclohexanol	X						
Acetophenone	X						
Possible C_5 Diol	X						
Possible Propyl ether	X						
C_{11} or C_{12} Acid, Methylester	X						
Phenol	X						
Possible Dimethoxy propane		X					
Diodomethane (AKA Methylene Iodide)		X					
2-Cyclohexen-1-01		X	X	X			
Bicyclo/3.1.0/hexane-3-one		X					
1-Bromo-2-chloro-cis-cyclohexane		X					
2-Chloro-trans-cyclohexanol		X					
2,5-Diethyl-tetra hydrofuran		X					
Dimethoxy methane or Trimethoxy methane		X	X	X		X	
C_4H_3Cl e.g. 1-chloro-2-1-buten-3-yne		X					
2-Ethoxy-1-methoxy-ethoxy ethane			X				
5-Methyl-1,2-hexadiene			X				
1-(2-Methyl-2-cyclopenten-1-yl)-ethanone			X				
C_8H_4O ketone				X			
Butyl oxyrane				X			
2-Imidazolidinone						X	
Vinyl Acetate						X	
C_4H_3Cl (e.g.) Chloro butatriene							X

TABLE B-18. ANALYSIS OF SELECTED ACIDIFIED PROCESS WATER EXTRACTS ON OV-17 GC COLUMN

Sample Extract	Identified Species (Estimated Concentrations µg/l water)
132/6-3-LEA-KD (settling pond overflow)	• Butyl naphthalene (4) (Plus possible an (1) Alkyl substituted naphthalene) • 1-Chloro-2,4-hexadine (0.5) • Unknown (3) • Freon Cmpd; $C_4Cl_4F_6$ (1)
132/6-5-LEA-KD (water to slag pond)	• Olefin or Ketone; C_8-C_{11} • Tetrachloropropane (possible) • 6-Chloro-n-ethyl-n'-(1-methylethyl-1,3,5-triazine-2,4-diamine • Octyldiphenylester of phosphoric acid.
132/6-6L-LEA-KD (acidified extract of liquid portion of inlet scrubber slurry)	• Freon; $C_4Cl_4F_6$

represents a deviation from established Level 2 procedures outlined in Reference B-1. These samples were first acidified to pH 2 and extracted with methylene chloride. The samples were then adjusted to pH 7 and re-extracted with methylene chloride. A final extraction was made at pH 11. This reversal in pH adjustment order results in the possibility that some neutral compounds were extracted into the acid extract solution for analysis on the Carbowax/H_3PO_4 column. These neutrals are more suitably screened on the OV-17 column. As a result, the acid pH extracts were also screened on the OV-17 column to search for neutral compounds. The discussion below discusses the results of these additional analyses.

Acidified Process Water Extracts--The results of the GC/MS screening analysis of extracts from the acidified process water samples are presented in Table B-17. These results were obtained using the Carbowax 20M-phosphoric acid column. In general, the detected compounds consist of oxygenates such as ketones, alcohols, ethers, and cyclic ethers. Some of these are lightly halogenated. One carboxylic acid, 2-ethyl hexanoic acid, and phenol were seen in these samples. Some unsaturated hydrocarbons were also identified.

Each of the acidified process water samples was generally found to contain compounds not found in any of the other acidified water extracts. However, two compounds were common to two or more samples. They were 2-cyclohexenol and a di- or tri-methoxy methane.

The mixture of compounds from extracts of the acidified process water and slurry liquid samples were not well resolved using the Carbowax 20M/phosphoric acid column. The resulting chromatograms had high backgrounds and broad peaks indicative of complex mixtures. Estimates of concentration levels of the individual compounds believed to exist in these extracts proved too unrealistic because of the high degree of background interference. Figure B-5 is a GC/MS total ion chromatogram for the acidified extract of the 132/6-3 process water stream. The incomplete peak separation is evident. If one makes a worst case assumption that some of the biggest peaks in these chromatograms are single compounds, then the highest concentrations for any

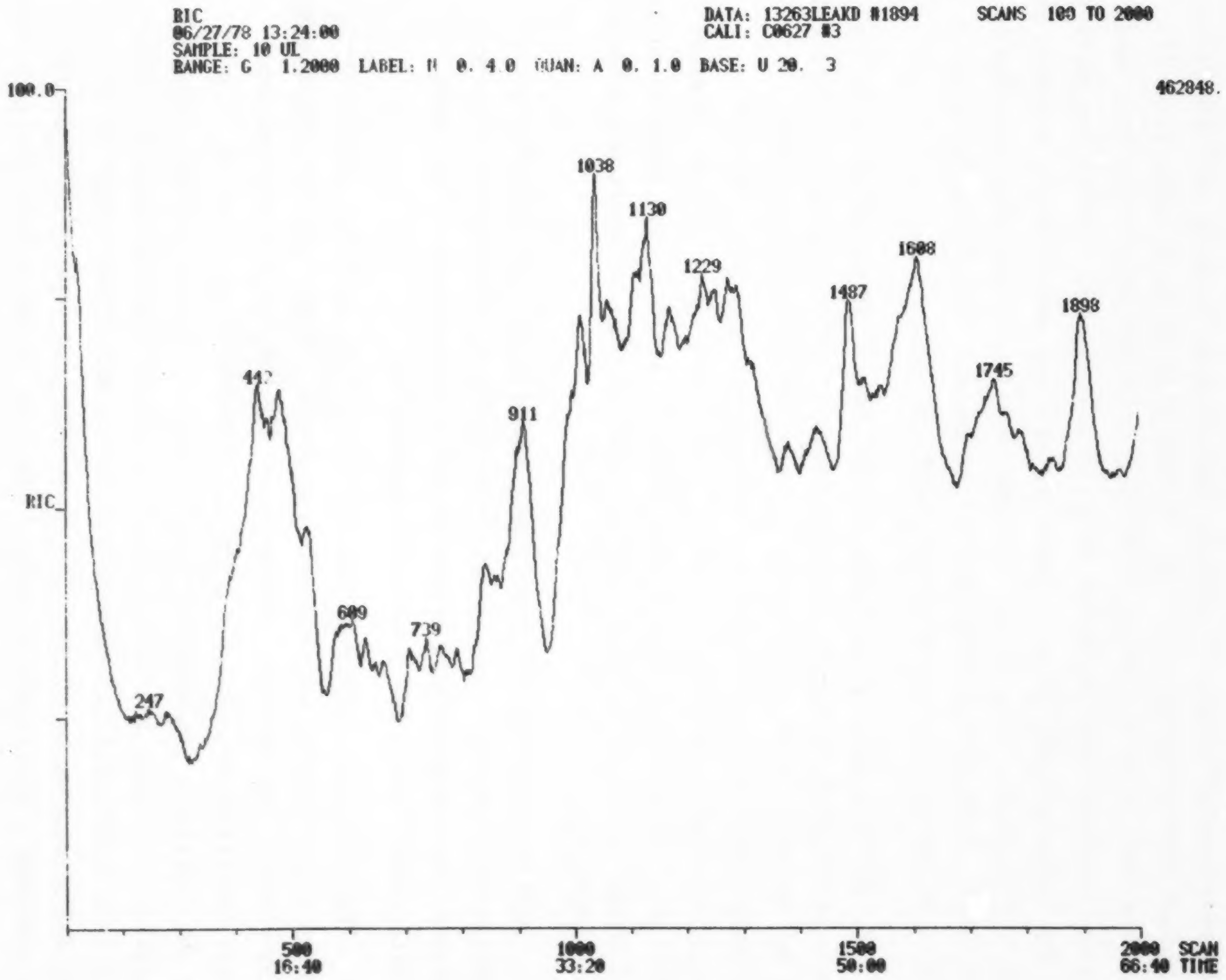


Figure B-5. Total ion chromatogram of concentrated extract of acidified process water sample one compound in these process waters would not exceed 10 to 15 micrograms per liter of water (µg/ℓ).

Three acidified water extracts were selected for additional GC/MS analysis on the OV-17 GC column intended for analysis of base/neutral compounds. The three selected samples are identified in Table B-18 along with compound identifications. It is interesting to note that there is no agreement in the qualitative identifications between the data for the same sample run under different GC conditions. The computerized data enhancement and library search results on the acidified extracts run on the Carbowax 20M/Phosphoric acid column should be considered more suspect. This is because of the high backgrounds and compound interferences are causes of incorrect background subtraction. No additional analysis have been carried out on the acidified process water extracts at this time due to budget and schedule limitations as well as the relatively insignificant estimated concentrations being observed.

Neutral and Basic Process Water Extracts--The results of the GC/MS analysis of the neutralized and basic process water extracts are presented in Table B-19. The six or seven compounds for which reasonable identifications exist are ketones, a di-acid ester, an aliphatic hydrocarbon and an aromatic hydrocarbon. Three ketones are common to at least two samples. The remaining compounds are found in individual samples.

Several of the samples did not contain compounds at detectable or identifiable levels. They are:

- 132/6-1-LEN
- 132/6-1-LEB
- 132/6-2-LEB
- 132/6-3-LEN
- 132/6-3-LEB
- 132/6-6L-LEN
- 132/6-7L-LEN

TABLE B-19. NEUTRAL AND BASIC PROCESS WATER EXTRACTS (CONCENTRATION, µg/l OF WATER SAMPLE)

	132/6-2-Neut	132/6-4-Neut	132/6-4-Basic	132/6-5-Neut	132/6-5-Basic	132/6-6L-Basic	132/6-7L-Basic	132/6-6S
3-Methyl-2-cyclohexen-1-one (Also called Diacetone)	X	2^{*}	X	X	X			
8-Methyl-3A-dihydro naphthalene-one			X	X				
3A,7A Dihydro-5-methyl indene-1,7(4H)-dione		$0.3^{\dagger}$	X	X				
C6 Nitrile or C5 Alcohol			X					
Di-2-Ethylhexil ester of Nonane dioic acid		$2^{\ddagger}$						
Possible 1-(4-Chlorophenyl)-1,4-Dihydro-2,3-biphenyl Quinoline				X				
Unknown						X		
2,2,5,5-Tetramethylhexane							X	
A Freon, e.g., 1,1,3,4-Tetrachloro-1,2,2,3,4,4-Hexafluoro Butane							X	
Diphenyl Heptane (Possible)							X	
Mixture of Trichloro propenes								X
Dimethylhexane								X
4-Methyl-2-propyl pentanol								X
C_9 or C_{10} branched hydrocarbon								X
Trimethylhexane								X
C_{10} Hydroxylamine								X
Di-tert-butyl-methylphenol (BHT)								X
Freon: $C_4Cl_3F_7$ or $C_4Cl_4F_6$								X
1,1-Diphenyl-3-methylbutane								X
1,1,6,6-Tetraphenylhexane								X

X = Compound Detected in Sample Extract.

* DMEG Value for Butanone is 6×10^6 µg/l.

† DMEG Value for Indene is 4×10^4 µg/l.

‡ No DMEG Value is given for Acid Esters.

Part of the reason why these samples did not contain any significant material may be due, at least in part to the reversed extraction sequence (acidified first) in which compounds normally found in the neutral extracts were found in the acidified estracts. This appears to be borne out by the results shown in Table B-16 for the acidified extracts. Many apparent neutral compounds are found there. The concentration in the final concentrated water extracts at which a compound would have to be present in a sample in order to be detected is estimated to be 3 μg/ml. This corresponds to a water concentration of 3 μg/ℓ.

The neutral extract of process water sample 4 was additionally analyzed with an internal standard to estimate the concentration of the detected species. The concentrations for the three compounds identified in the sample are shown in Table B-19. The presence of compounds found in the remaining samples are indicated by an X.

The solids portion of the 132/6-6 and 132/6-7 slurry samples were also extracted with methylene chloride after separation from the slurry. These extracts were also screened on the GC/MS using the OV-17 column. The extract of the solids from the process slurry sample 6 had a mixture of hydrocarbons, 2 halogenated species, an alcohol, a hydroxylamine and BHT, a common antioxidant (Table B-19). The slurry solids extract from process stream 7 had three compounds at levels too low to identify above sample background. These levels were not specifically determined but inspection of peak areas for the 3 unknowns are estimated to be very much less than a water concentration of 1 μg/ℓ.

APPENDIX C

LA CYGNE INORGANIC ANALYSIS RESULTS

The comparative assessment tests conducted at the La Cygne Power Plant were designed to study the effect of emission control devices on the flue gas composition. As part of this program, Level 1 and comprehensive Level 2 sampling and analysis procedures were used to study the inorganic compounds in the flue gas streams. The Level 2 sampling consisted of using a modified Method 5 train for particulate matter in the flue gas and the controlled condensation system for the H_2SO_4 content of the flue gas.

After the Level 1 data was reviewed, specific analytical techniques were used as part of the comprehensive Level 2 approach. These methods included:

- Thermogravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) — Used to determine drying temperatures or stability data.
- Polarized Light Microscopy (PLM) — Used visually to identify materials present in the sample.
- Atomic Absorption Spectroscopy (AAS) — Used to determine accurate inlet/outlet concentration of elements.
- Particle Induced X-Ray Emission (PIXE) — Used to determine elemental composition of individual impactor stages.
- Fourier Transform IR (FTIR) — Used to identify inorganic compounds from specific IR band correlations.
- X-Ray Diffraction (XRD) — Used to directly identify crystalline material in the solid samples.
- Electron Spectroscopy for Chemical Analysis (ESCA) — Used to study the surface and sub-surface sulfur concentrations and oxidation state of bulk samples.
- Secondary Ion Mass Spectrometry (SIMS) — Used to study the surface and sub-surface composition of bulk samples.
- Scanning Electron Microscope with Energy Dispersive X-Ray Fluorescence (SEM-EDX) — Used to obtain high resolution photographs and elemental composition of single particles.

In addition to these instrumental methods, specific anion analyses for Cl^-, F^-, and $SO_4^=$ were run on the CCS train samples.

The following sections will discuss the results from TGA/DSC, PLM, SEM/EDX, SSMS, XRD and MRI impactor analyses. PIXE, FTIR, and SIMS analyses did not give meaningful results and are not reported here. The results of other analytical techniques (AAS, ESCA, and specific anion analyses) have been discussed in the text.

RESULTS OF ANALYSES

Complete sets of samples were available for the 135 run. Only this sample set was analyzed. The following sections contain the data from each of the methods employed for each sample analyzed. In some cases, two or more methods will be discussed together for comparison purposes.

TGA/DSC Results

Differential Scanning Calorimeter (DSC) measures the energy required to maintain a sample at the same temperature as a reference material as both temperatures are raised. In this way the area under the peak is a direct measure of the enthalpy of a physical or chemical change. Thermogravimetric analysis (TGA) measures weight gain or loss as the temperature is steadily increased. By comparing DSC and TGA results, phase changes can be differentiated from chemical decomposition.

TGA and DSC's were run on: 133-18-BA (bottom ash), 135-6 (scrubber slurry in), 135-7 (scrubber slurry out), 135-LF (lime feed), and 135-OUT-CYC (SASS cyclone catch). In addition TGA's were run on 135-IN-PF (SASS filter catch), 135-IN-PFa (SASS filter catch; "a" denotes second filter used during run), 135-OUT-PF, and 135-IN-CYC. The analyses were run using DuPont 950 TGA/DSC system in a N_2 atmosphere at temperatures up to 650°C.

Table C-1 summarizes the results of the TGA and DSC results. The inlet cyclone and filter catches show similar weight loss profiles. The inlet filter samples show an additional feature on the TGA at 170°C which does not appear in the cyclone TGA. While both inlet filter samples have the same profile, the weight loss for 135-IN-PF is over twice as much than 135-IN-PFa. Also the inlet filters have more of a weight loss than the inlet cyclone catch.

TABLE C-1. TGA/DSC RESULTS

Sample	DSC	TGA
135-IN-CYC	No significant features	- Slow loss of weight (1.3%) up to 550°C. Slight increase in weight loss up to 650°C.
135-IN-PF	Not Run	- 20% weight loss up to 175°C. - An additional weight loss of 8% until ∿525°C. - Sharp weight loss after 550°C.
135-IN-PFa	Not Run	- Loss of 9.7% weight up to 170°C. - An additional 2.8% lost up to 550°C. - Sharp increase in weight loss at up to 650°C limit
135-OUT-CYC	- Three large endothermic peaks at 87°C, 120°C, and 190°C. Small endothermic peak at 220°C.	- Large weight loss (36.7%) over a range of 50°C to 350°C. - Sharp increase in weight loss at 550°C.
135-OUT-PF	Not Run	- Loss of 6.3% weight up to 60°C. - Slow, consistent weight loss (5%) from 60°C to 475°C.
133-18-BA	No significant features	- Loses no weight from 25°C to 650°C.
135-6	- Small endothermic peak at 113°C	- Slight weight loss starts at ∿525°C.
135-7	- Small endothermic peak at 128°C and a large, sharp endothermic peak at 407°C	- 0.8% weight loss up to 360°C. - 2.1% lost from 395 to 420°C. - Stable to 600°C.
135-LF	- Possible endothermic peak at 33°C	- Weight loss of 1.9% at 50°C. - Slow weight loss from 400° to 650°C (<3%) — possibly due to instrument interference

At the scrubber outlet the cyclone sample weight loss is far greater than the filter. The DSC of the outlet cyclone shows three large endothermic peaks at 87°C, 120°C, and 190°C with several smaller shoulders at 140°C and 230°C. The major peaks roughly correspond to the dehydration of $CaSO_3 \cdot 1/2\ H_2O$ (100°C), $CaSO_4 \cdot 2H_2O$ (to the half hydrate - 128°C) and $CaSO_4 \cdot 1/2\ H_2O$ (163°C). The profiles for the outlet samples may indicate that the outlet material is modified with respect to the inlet particulate.

DSC can be influenced by the heating rate. At high heating rates the sample temperature may tend to lag behind the temperature of the reference material for endothermic reactions. The DSC spectra of the 135-OUT-CYC was repeated at a heating rate of 2°C/min (original 10°C/min). The scan is quite different, showing peaks at 47°C, 94°C, 160°C, and shoulders at 115°C and 175°C. The 47°C peak is probably due to surface water and baseline drift. The 94°C and the 160°C may correspond to the $CaSO_3 \cdot 1/2\ H_2O \rightarrow CaSO_3$ and the $CaSO_4 \cdot 1/2\ H_2O \rightarrow CaSO_4$ dehydrations. The shoulder at 115°C might be due to the dehydration $CaSO_4 \cdot 2H_2O$. The 175°C shoulder is unidentified, but may represent a phase change of $CaSO_4$ between α & β forms or a reaction of an unidentified material.

PLM and SEM-EDX Results

Polarized light microscope analyses were completed on the following samples:

133-18-BA
135-IN-CYC
135-IN-PF
135-IN-PFa
135-IN-PFb
135-LF
135-6
135-7
135-OUT-CYC
135-OUT-PF
135-OUT-PFa

Where SEM-EDX analysis emphasizes the PLM results, the photos are used to illustrate the result.

Size Distributions

Where possible a size distribution of each sample was determined. Materials which appeared to have crystallized on the filter or within a sample after collection were not included in the size distribution.

The outlet filter samples, 135-OUT-PF and 135-OUT-PFa were composed almost exclusively of these crystallized materials. For this reason, no size distribution of these samples was determined.

All of the particles in 133-18 are too large to be sized with optical microscopy. The samples containing limestone as the major component, 135-LF and 135-6 are composed of a large number of particles which are too big to be sized with optical microscopy. With such a great size range (<1μm to almost a centimeter in diameter) a much larger sample is needed to obtain a representative size distribution and other sizing techniques such as sieving would need to be employed.

No size distribution of these samples was obtained with optical microscopy.

The size distributions are presented in Table C-2. The arithmetic mean diameter of the particles in these samples has been calculated and is shown in Table C-2 as well.

Composition

The composition of each of the eleven samples submitted are shown in Table C-3. Samples were desiccated and mounted in a 1.515 refractive index oil for the analysis. Samples which were analyzed directly on glass fiber filters were: 135-IN-PF, 135-IN-PFa, 135-IN-PFb, 135-OUT-PF, and 135-OUT-PFa.

These samples were desiccated and then, using a needle, a portion of the sample was scraped off of the filter onto a slide. The filter and the powder scraped off were mounted separately for the analysis.

In the samples collected on filters and in the 135-OUT-CYC sample, there were three different types of crystals which were formed in the various samples. These can be seen in Figure C-1. They are:

> Type 1: This crystal form was found in all five of the filter samples. It is in the form of spherulites with a birefringence greater than 0.08. The spherulites are made up of prism shaped rods radiating from a central point. One refractive index is slightly greater than 1.515 and the other is considerably greater than 1.515. The rods show parallel extinction.

TABLE C-2. OVERALL SIZE DISTRIBUTIONS

Size Ranges(μm)	135-IN-CYC	135-IN-PF	135-IN-PFa	135-IN-PFb	135-OUT-CYC
<1.0	16.2%	54.9%	53.1%	62.2%	40.9%
1.0-2.0	19.8%	34.6%	34.9%	28.6%	28.8%
2.0-3.0	21.6%	9.3%	9.3%	7.6%	15.6%
3.0-4.0	14.4%	0.2%	2.7%	1.3%	8.6%
4.0-6.0	14.4%	0	0	0.4%	4.7%
6.0-8.0	4.5%	0	0	0	1.2%
8.0-10.0	4.5%	0	0	0	0.4%
10.0-14.0	2.7%	0	0	0	0
14.0-20.0	1.8%	0	0	0	0
>20.0	0	0	0	0	0
Arithmetic Mean Diameter	3.5 μm	1.0 μm	1.1 μm	1.0 μm	1.5 μm

	135-7
<3.2	32.5%
3.2-6.4	26.3%
6.4-12.8	23.0%
12.8-19.2	13.9%
19.2-32.0	3.8%
32.0-48.0	0.5%
>48.0	0
Arithmetic Mean Diameter	7.7 μm

TABLE C-3. COMPOSITION OF SAMPLES

COMPONENTS	133-18	135-IN-CYC	135-IN-PF	135-IN-PFa	135-IN-PFb	135-LF	135-6	135-7	135-OUT-CYC	135-OUT-PF	135-OUT-PFa
Limestone						95% +	98% +	45-60%			
Flyash		80-95%	35-50%	35-50%	40-55%			5-10%	15-30%		
Magnetite	<2%	5-15%						5-10%			
Partially Combusted Coal		<2%	<2%	<2%	<2%			<2%	<2%		
Crystallized Minerals										95%	95% +
Type I			50-65%	50-65%	40-60%						
Type II									70-85%		
Type III											
$CaSO_3 \cdot 1/2\ H_2O$								30-45%			

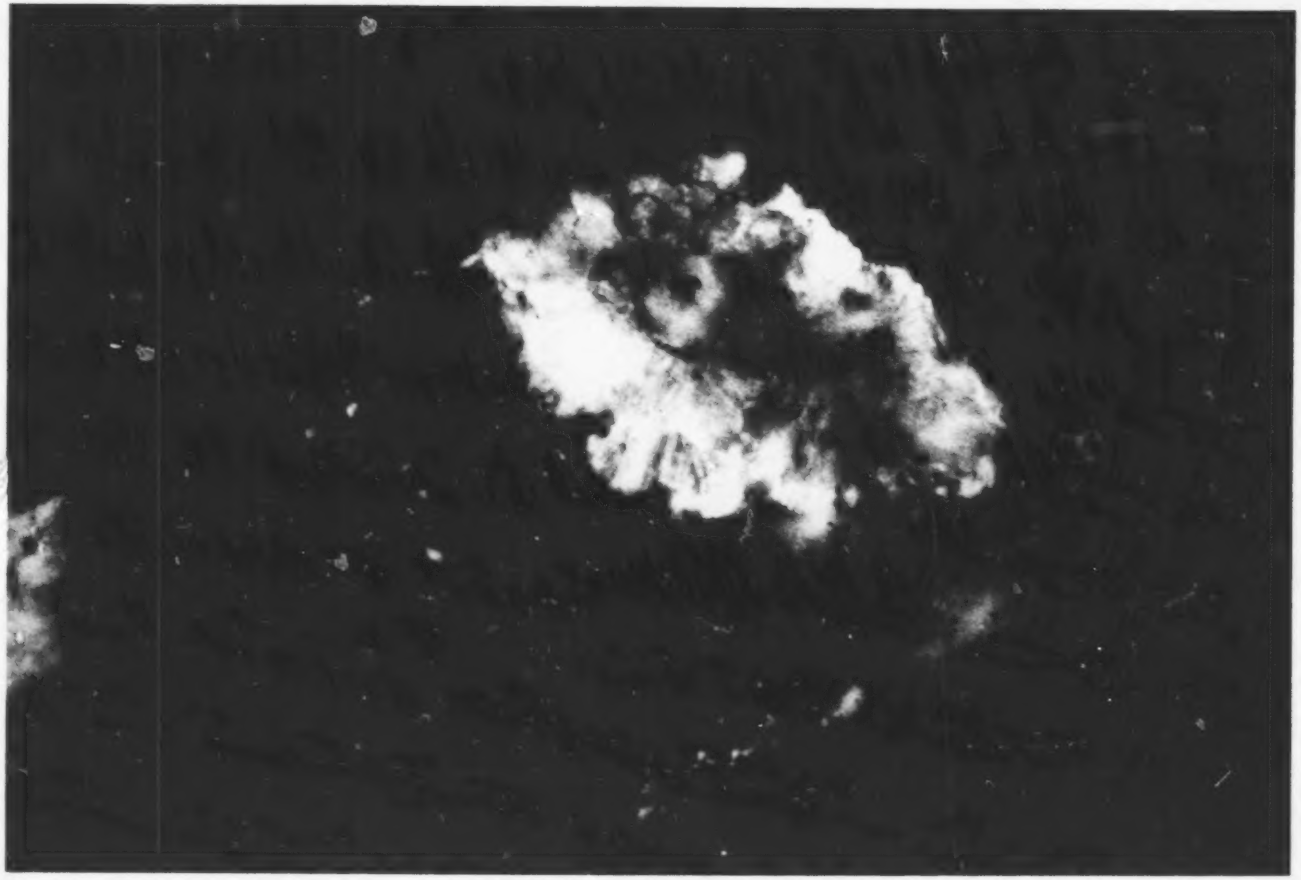


Figure C-1 - 135-OUT-PFa Showing the Three Types of Crystallized Minerals Found in These Samples; Partially Uncrossed Polars (PUP), 131X

Type 2: The second type of crystallized mineral is either in thin plates or irregular round chunks. In the photomicrograph it is the mottled angular plate upon which the spherulites are sitting. It has a birefringence of approximately 0.01. The refractive indices are difficult to determine since the plates are composed of many tiny, independent crystals. This mineral type is found in all three outlet samples but in none of the others.

Type 3: These are the brown nodules seen in the photomicrograph. They are brown in transmitted light and white in reflected light. Air bubbles within the nodules are probably responsible for the white color. They also show a maltese cross on their surfaces with crossed polars. The refractive indices of these particles are between 1.515 and 1.600 (closer to the latter). They have very low birefringence, probably less than 0.010 and show parallel extinction. These nodules are only found in the filter outlet samples, 135-OUT-PF and 135-OUT-PFa.

The above crystals will be refered to as Type 1, Type 2, and Type 3 in the text.

Other than the crystals, the most frequently encountered emissions are flyash and magnetite. Partially combusted coal is seen in most samples but always as a minor component. Calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2\ H_2O$) laths were found as a major component of the scrubber cake. Limestone was also found in the scrubber cake.

Descriptions of the individual samples follow.

133-18-BOTTOM ASH

The particles in this sample were much too large to be analyzed with optical microscopy. For this reason, a small portion of the sample was crushed with a mortar and pestle for the analysis.

The slag is composed of glassy, isotropic particles which show concoidal fracture (Figure C-2). They have a refractive index of about 1.595 and are an olive-green color. The glassy nature of the slag indicates that the temperatures reached were sufficient to vitrify the mineral contaminants of the coal.

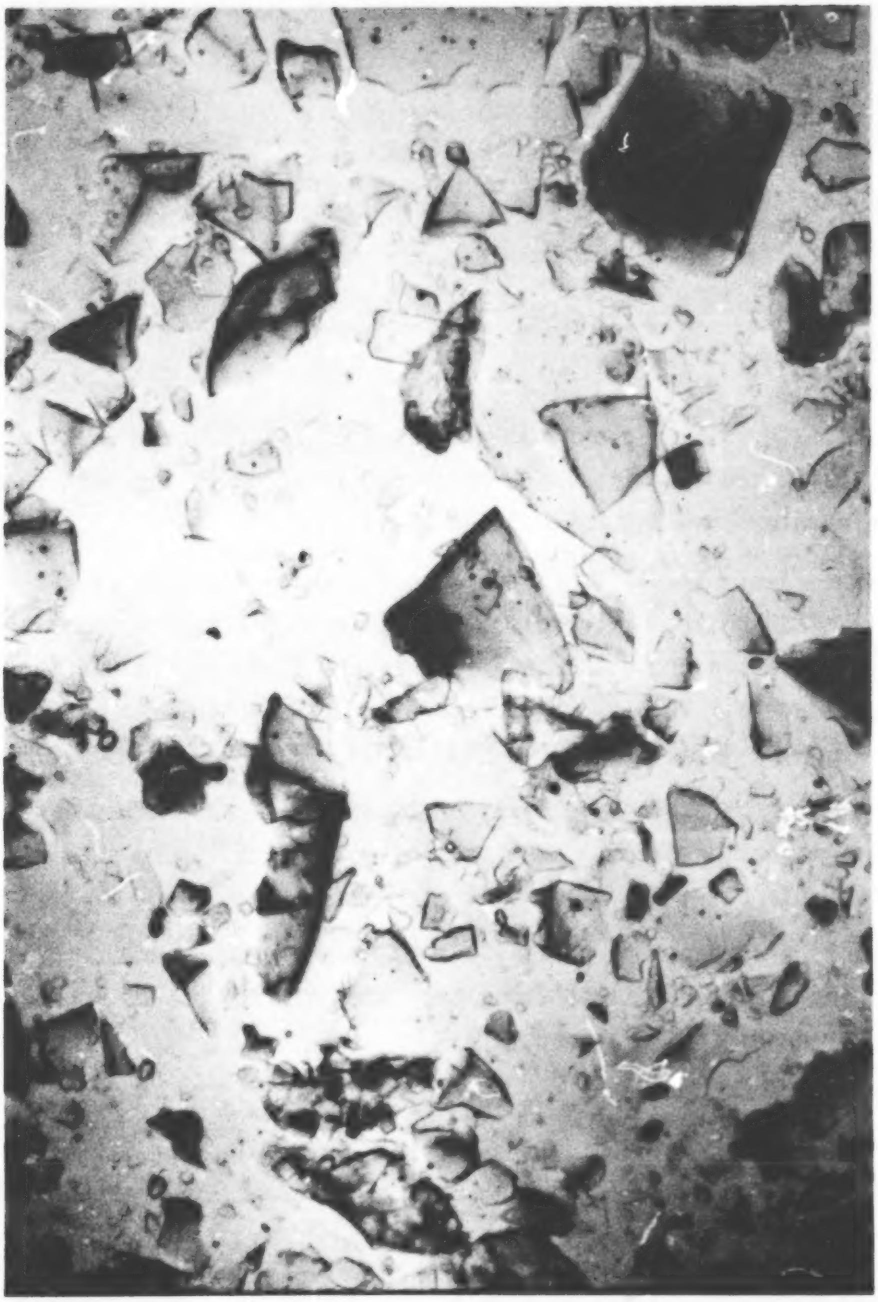


Figure C-2 - 133-18 Showing the Crushed Slag; Plane Polarized Light (PPL); 51X

Incorporated within the slag is magnetite, most of which is less than 1μm in diameter. These spheres are speckled throughout the glassy slag. Irregularly shaped magnetic fragments are also associated with the slag.

135-IN-CYC-INLET CYCLONE

Components	Concentration	Average Diameter (μm)	Size Range
Flyash	80-95%	4	<1-35
Magnetite	5-15%	12	5-25
Partially combusted coal	2%	15	<1-100

This sample is almost entirely composed of flyash and magnetite. Partially combusted coal is also present but it accounts for less than 2% of the sample mass (Figures C-3 and C-4).

80-95% of this sample is flyash with a average diameter of about 4μm. These flyash spheres range in color from clear to black-brown. Most of the flyash is golden brown and some spheres are plerospheres and many contain a few large air bubbles. Figure C-5 is a SEM photo of a broken cenosphere. Figure C-6 is a higher magnification of same.

Magnetite spheres compose 5-15% of this sample mass. These are shiny black magnetic spheres. The smallest magnetite sphere seen was about 5μm in diameter; the largest about 25μm.

The coal fragments are partially combusted and very lacey. Even the large fragments are very light since they are only the porous, combustion residue of the original coal particles.

135-IN-PF

Components	Concentration	Average Diameter (μm)	Size Range (μm)
Flyash	35-50%	1	<1-6
Partially combusted coal	<2%	3	<1-15
Crystallized minerals:			
Type 1	50-65%		

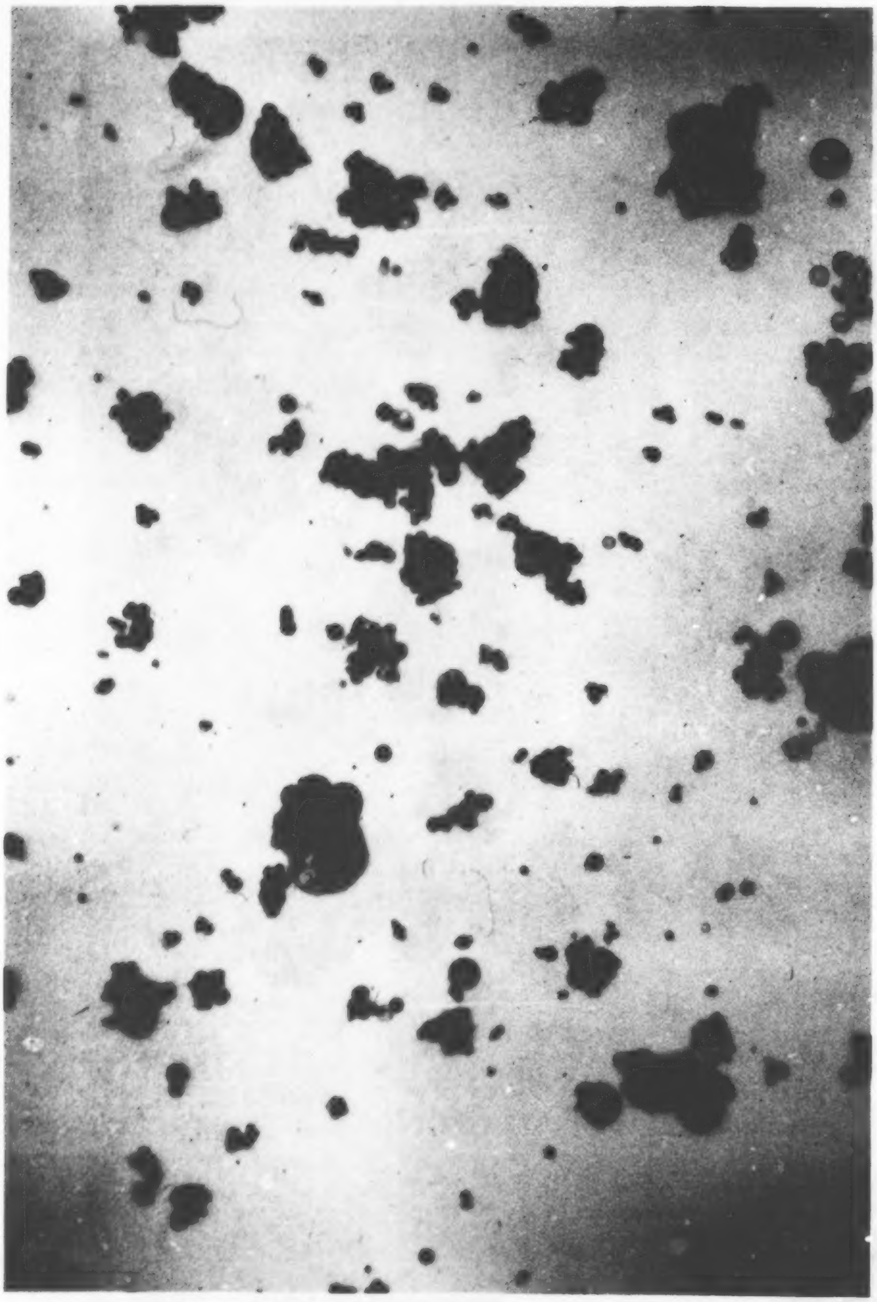


Figure C-3 - 135-IN-CYC Showing Flyash, Magnetite, and Partially Combusted Coal PPL, 51X.

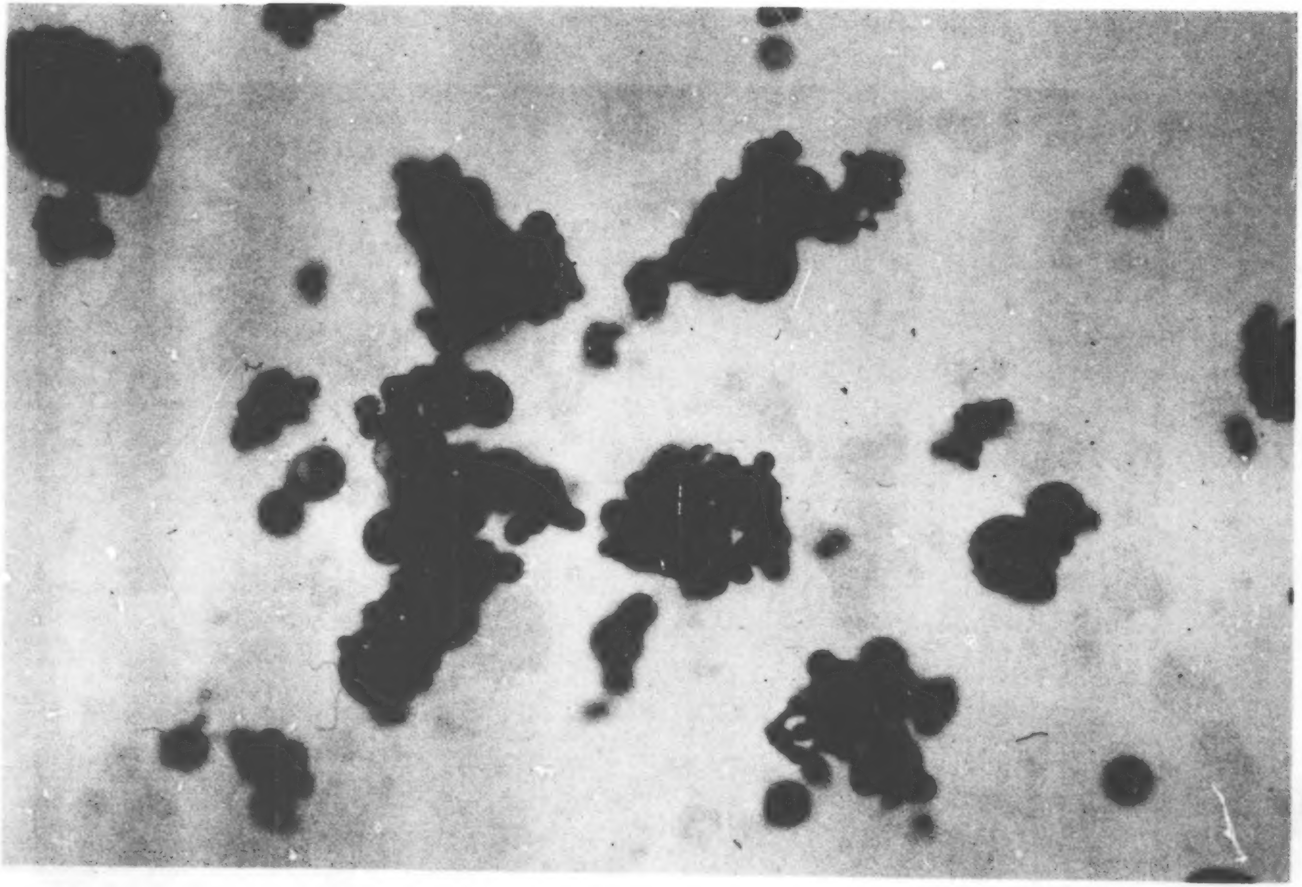


Figure C-4 - 135-IN-CYC Showing the Same Field of View as Figure C-3 but at a Higher Magnification; PPL, 131X.

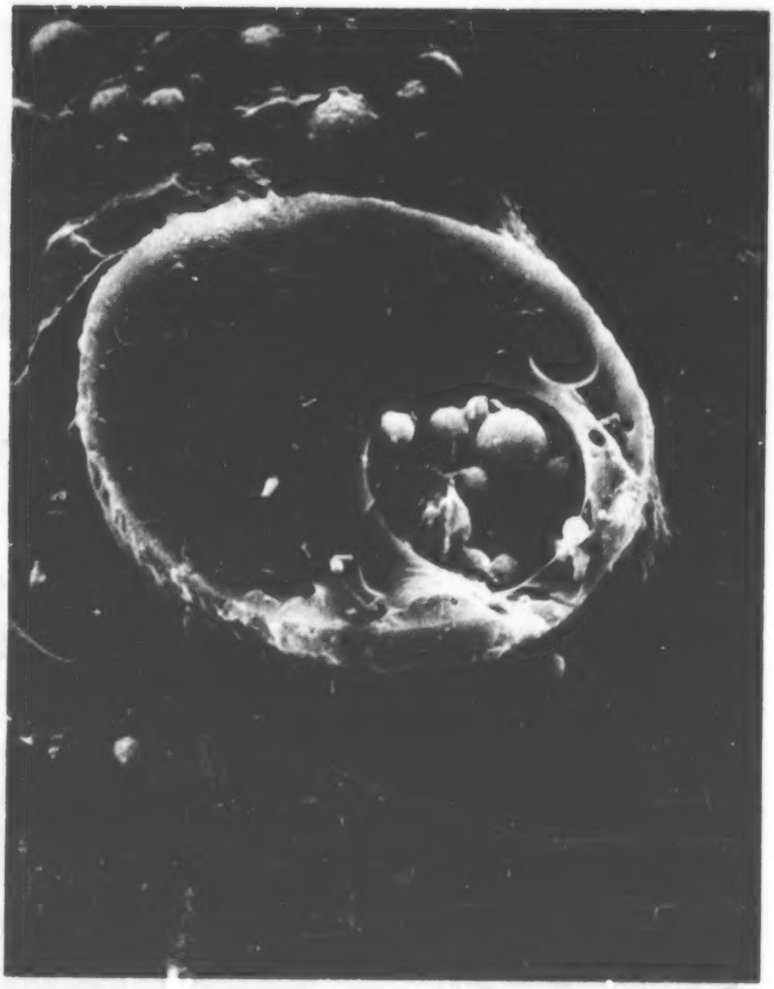


Figure C-5 - SEM Photograph (1400X) of 135-IN-CYC Showing Cenospheres and Air Pockets in Broken Cenosphere

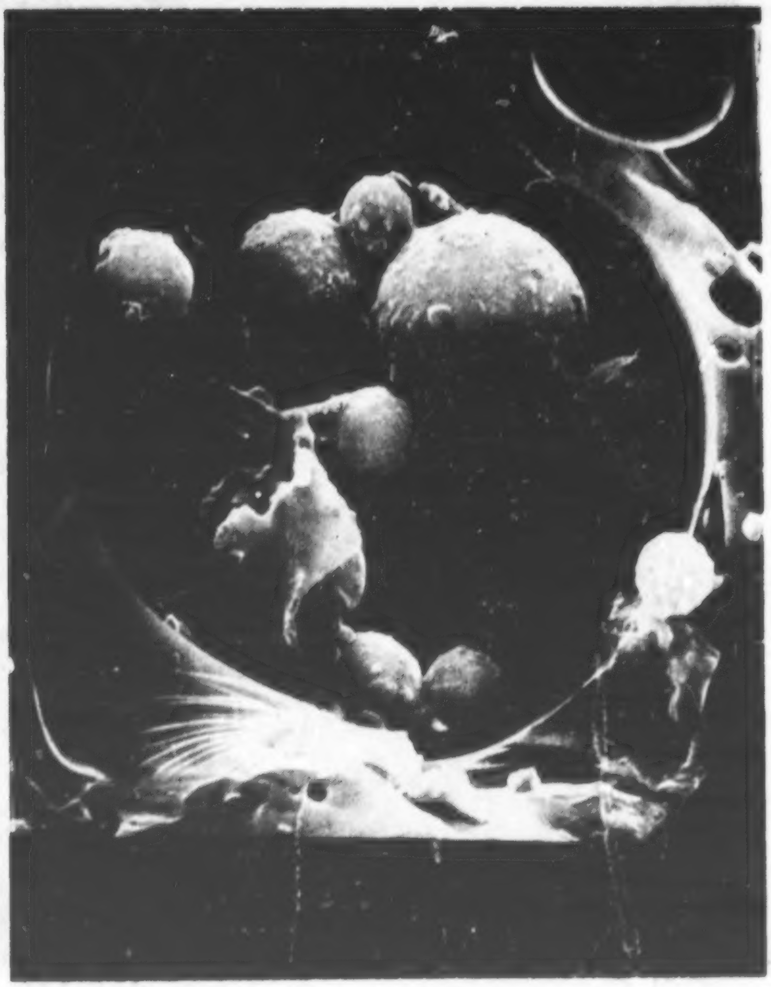


Figure C-6 - Closeup (4000X) of Smaller Cenospheres that Fill Into Fractured Cenosphere

The photomicrographs of this sample (Figure C-7) and of the other two inlet filter samples (Figures C-8 and C-9) are of the undesiccated samples. This is because after desiccation the particles agglomerated making dispersion impossible. After desiccating the samples, Type 1 spherulites was the major sample component. Since the photos are of wet samples, the particles shown do not include the soluble Type 1 spherulites.

By far the most numerous particulate found in this sample is flyash. Almost all of the flyash is less than 4μm in diameter. The average flyash diameter is about 1μm. The color of the glassy flyash spheres are primarily golden brown with a few spheres which are colorless, red, or brown.

Partially combusted coal was the only other combustion product detected. It is a minor sample component, not more than 2% of the sample mass. Magnetite which was 5-15% of the 135-IN-CYC sample is not present in this sample. This is probably because the magnetite spheres are too large and heavy to pass the cyclone.

135-IN-PFa, 135-IN-PFb-Filter Samples

	Concentration	Average Diameter (μm)	Size Range (μm)
135-IN-PFa			
Flyash	35-50%	1	<1-6
Partially combusted coal	<2%	3	<1-15
Crystallized Minerals:			
Type 1	50-65%		
135-IN-PFb			
Flyash	40-55%	1	<1-8
Partially combusted coal	<2%	3	<1-12
Crystallized minerals:			
Type 1	45-60%		

Both of these samples are similar in composition and particle size range to the 135-IN-PF sample. 135-IN-PFb seems to contain a slightly lower percentage of the spherulitic crystals (Figures C-10 and C-11) but this

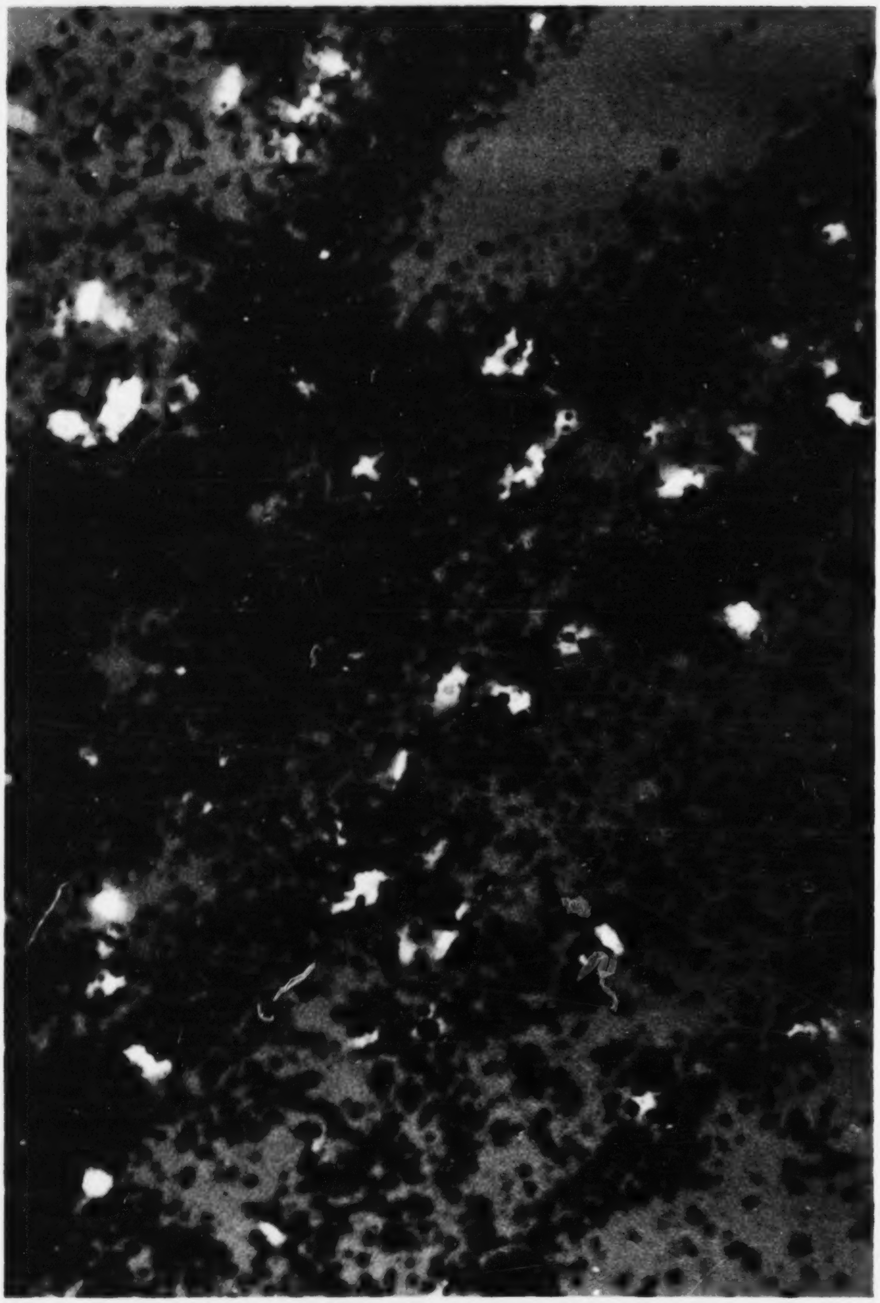


Figure C-7 - 135-IN-PF Before Desiccation, Shows Flyash; PUP, 131X.

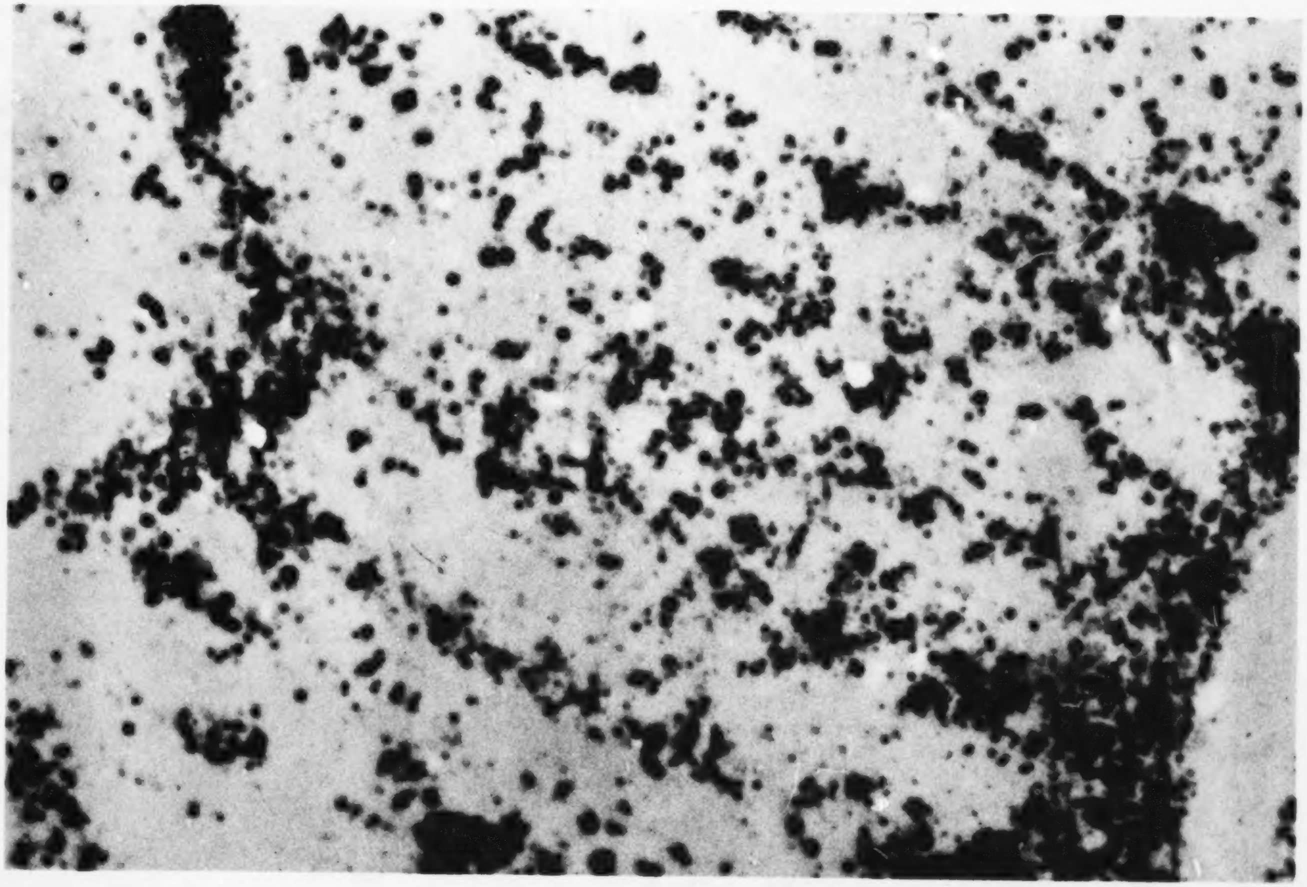


Figure C-8 - 135-IN-PFa Before Desiccation, Shows Flyash; PUP, 131X.

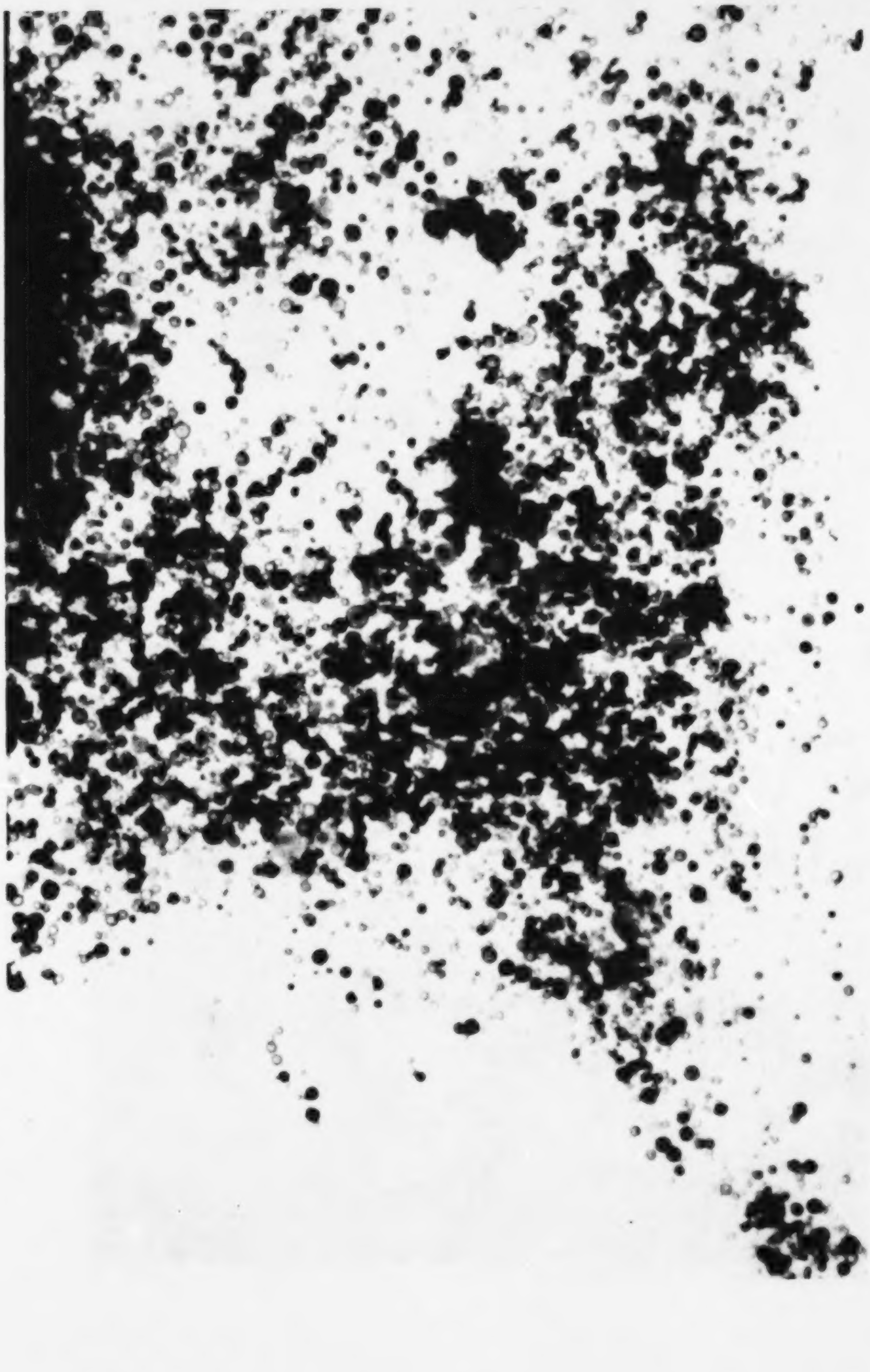


Figure C-9 - 135-IN-PFb Before Desiccation, Shows Flyash; PUP, 131X.

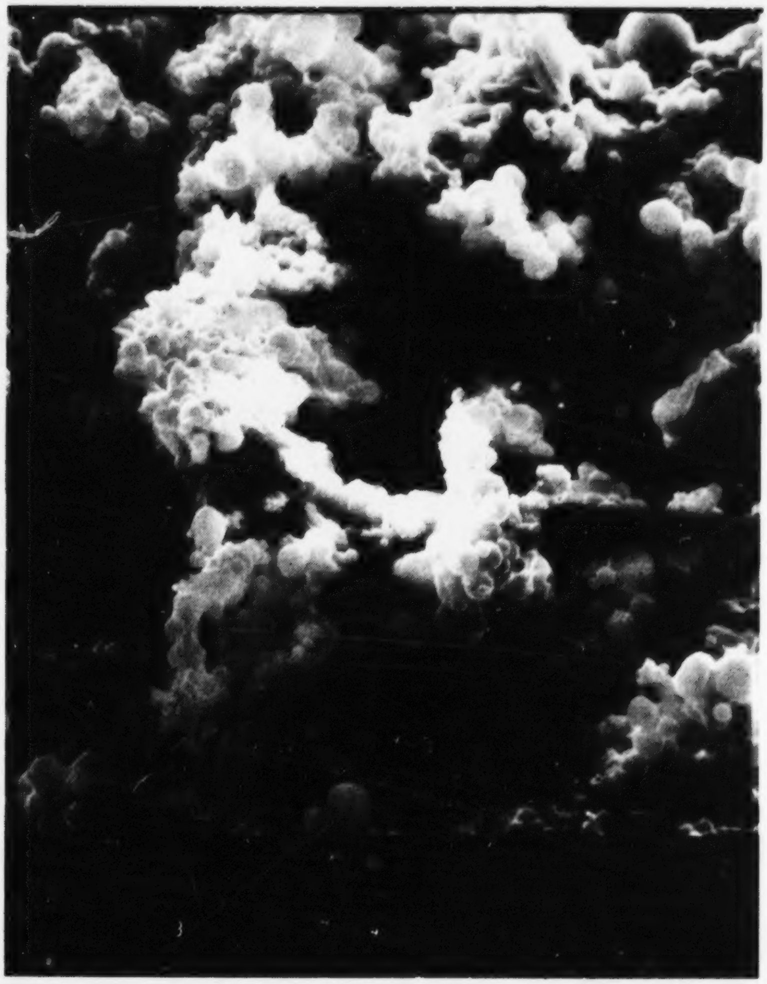


Figure C-10 - SEM Photograph of Section of 135-IN-PFa Filter Sample With Type I Crystal in Upper Right Hand Corner

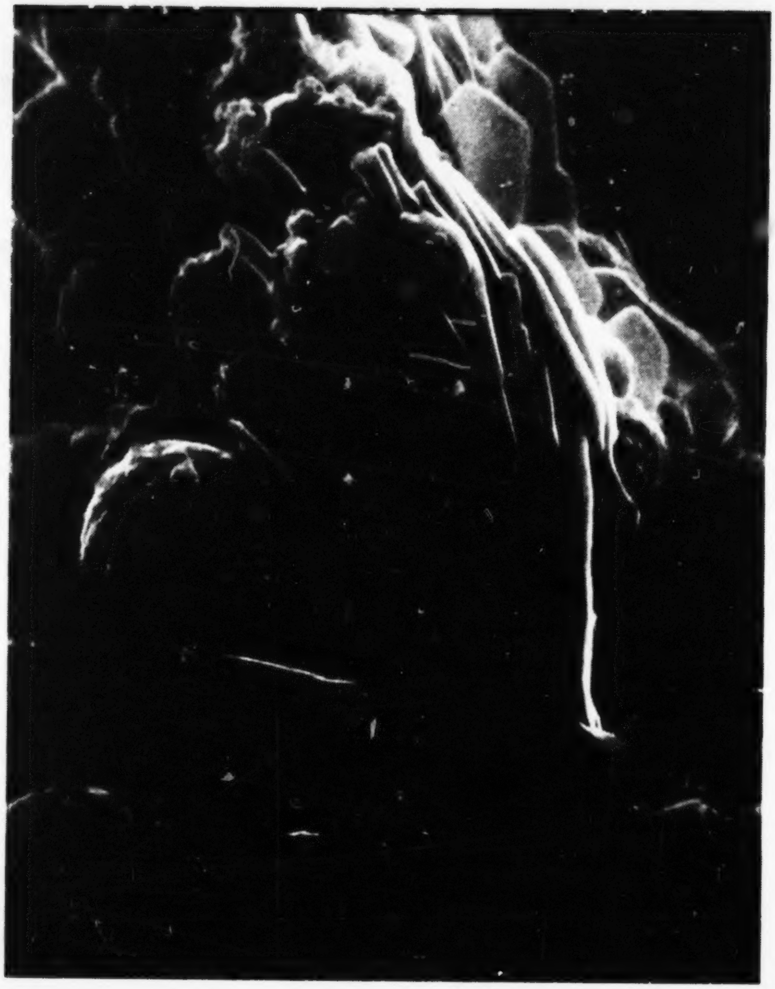


Figure C-11 - 9000X Enlargement of Type I Crystal in Figure 3.
EDX Analysis: High, Fe, Si, S; Medium Zn; Low K, and Ca

may only be the result of a possible difference in crystallizing conditions between the samples. The elemental analysis showed Fe, Si and S to be the major elements, Zn, K and Ca were also present. It could be possible that H_2SO_4 impinging on the flyash dissolved Fe and formed the crystals. However, the strong (30 kV) beam strength probably excited the flyash underneath the Type I crystals, which resulted in the apparent Fe line.

As in the 135-IN-PF sample, flyash is the most numerous particulate. The colors and modal size of the flyash spheres are approximately the same in all three samples. Even though spheres greater than 4μm in diameter are present, 99% of the flyash is less than 4μm in diameter.

Partially combusted coal, (average diameter: 3μm) is <2% of both samples. As in 135-IN-PF, no magnetite was seen.

135-LF-Limestone Feed

Probably greater than 95% of this sample is limestone. Other components can be regarded as contaminants and the degree of contamination is highly dependent upon which portion of the sample was used for the analysis. Approximately 10 slides were made. Several were made of a large crushed limestone "rock". The rest of the slides were prepared of the fine limestone dust in the sample.

The samples prepared from the crushed rock were almost exclusively composed of limestone (Figure C-12). Much less than 1% of these samples was contaminants. These contaminants were primarily quartz and clays and there was a very trace amount of coal or humus. These contaminants were probably those which adhered to the outside of the rock and are not incorporated within it.

The samples of dust or fine particles were much more heavily contaminated. Some samples contained as much as 10-25% contaminants. As in the crushed rock, clays and quartz were the predominant contaminants.

Most of the quartz fragments were heavily speckled with clays and humus and there are individual clay particles as well. Agglomerates of clay and quartz (Figure C-13) were commonly seen. A trace of coal (or humus) is present, too. In reflected light some of the limestone chunks have a yellow surface coating. This is probably a thin coating of hydrated iron oxide.

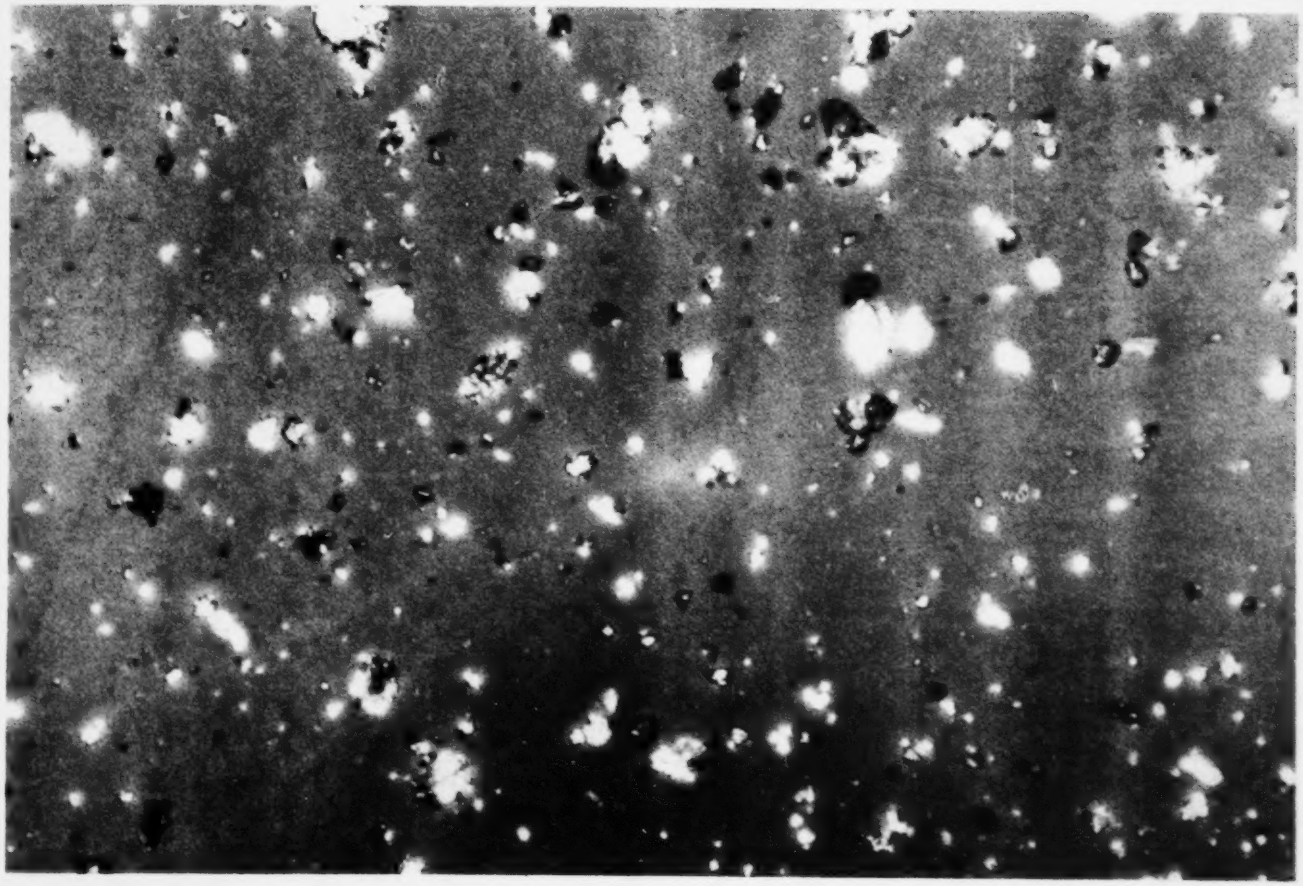


Figure C-12 - 135-LF Showing a General View of Crushed Limestone "Rock"; PUP, 51X.

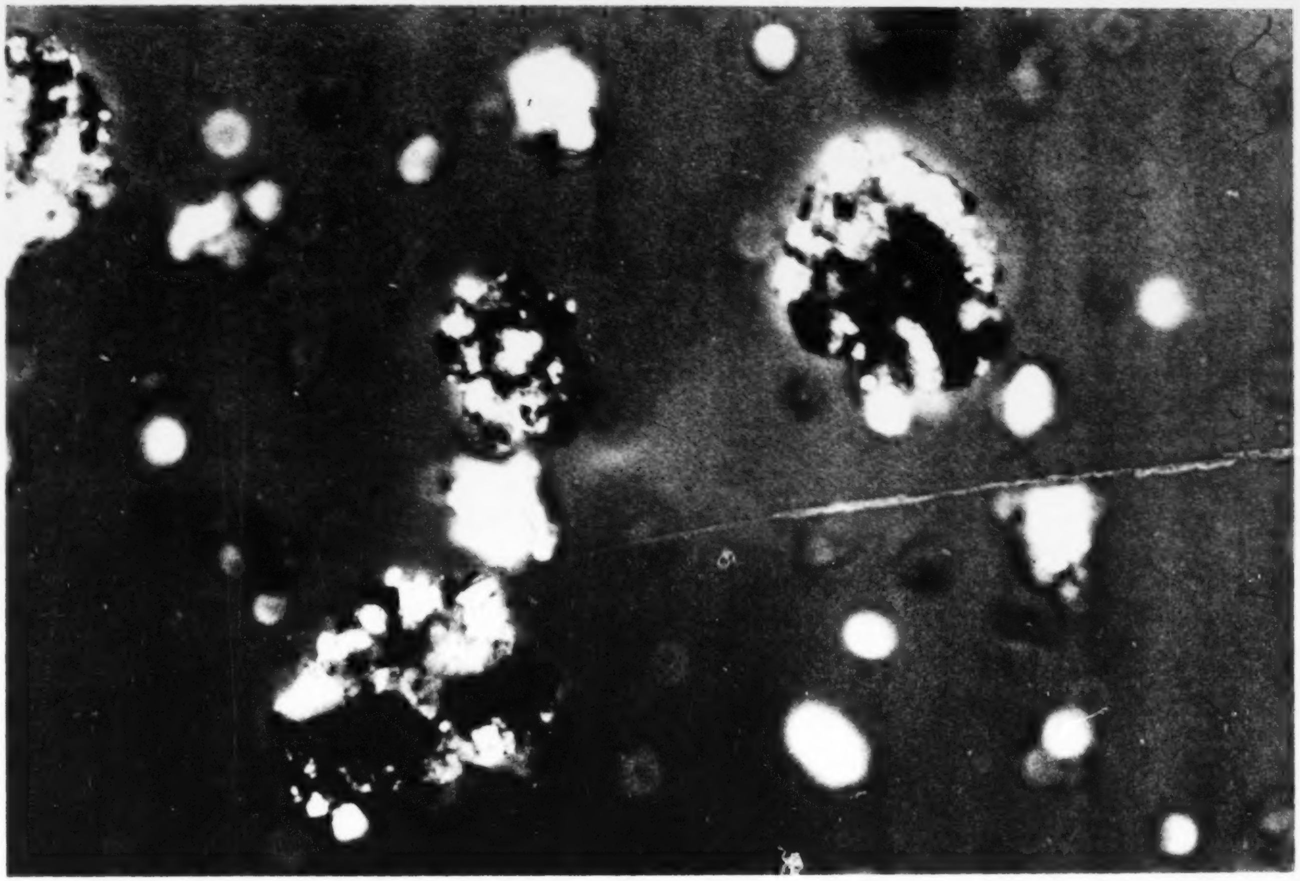


Figure C-13 - 135-LF Showing Soil Agglomerates Which Contaminate the "Dust" Samples PUP, 131X.

Determination of the actual percent of contaminants is impossible since they are so unevenly distributed within the sample received. By far the greatest sample mass is involved in the limestone "rock" and its purity would imply greater than 99% is limestone. However, if limestone dust is a large sample component, then the sample may not be this pure.

135-6-SLURRY IN

This sample of limestone (Figure C-14) seems to be much cleaner than the 135-LF sample. In no slide prepared of this sample were contaminants greater than 2% of the sample mass. In most samples, the contaminants were difficult to find and contributed considerably less than 1% of the mass.

The major contaminants found in 135-6 were humus, coal fragments, and quartz. Individual clay particles and soil agglomerates are much lesser contaminants than in 135-LF sample. Some of the limestone chunks have an iron oxide coating making them appear yellow in reflected light.

135-7-Scrubber Cake

Components	Concentration	Average Diameter (μm)	Size Range (μm)
$CaSO_3 \cdot 1/2\ H_2O$	30-45%	15 (length)	3-60 (length)
Limestone	45-60%	9	<1-200
Flyash	5-10%	5	<1-40
Magnetite	5-10%	20	5-80

The primary components are calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2\ H_2O$) laths and limestone (Figures C-15 and C-16). Though the laths appear to be more numerous, the limestone particles are generally larger and thereby contribute a greater mass to the sample.

The $CaSO_3 \cdot 1/2\ H_2O$ laths compose 30-45% of the overall sample mass. These laths are transparent and have refractive indices: $\alpha=1.596$, $\beta=1.598$, $\gamma=1.634$. The birefringence of the lath surface usually observed is about 0.028. The modal lath length is about 15μm though they range from 3-60μm in length. Most have about a 3:1 aspect ratio (length: width). The maximum thickness of a lath seen was only about 5μm - most were less than 2μm thick.

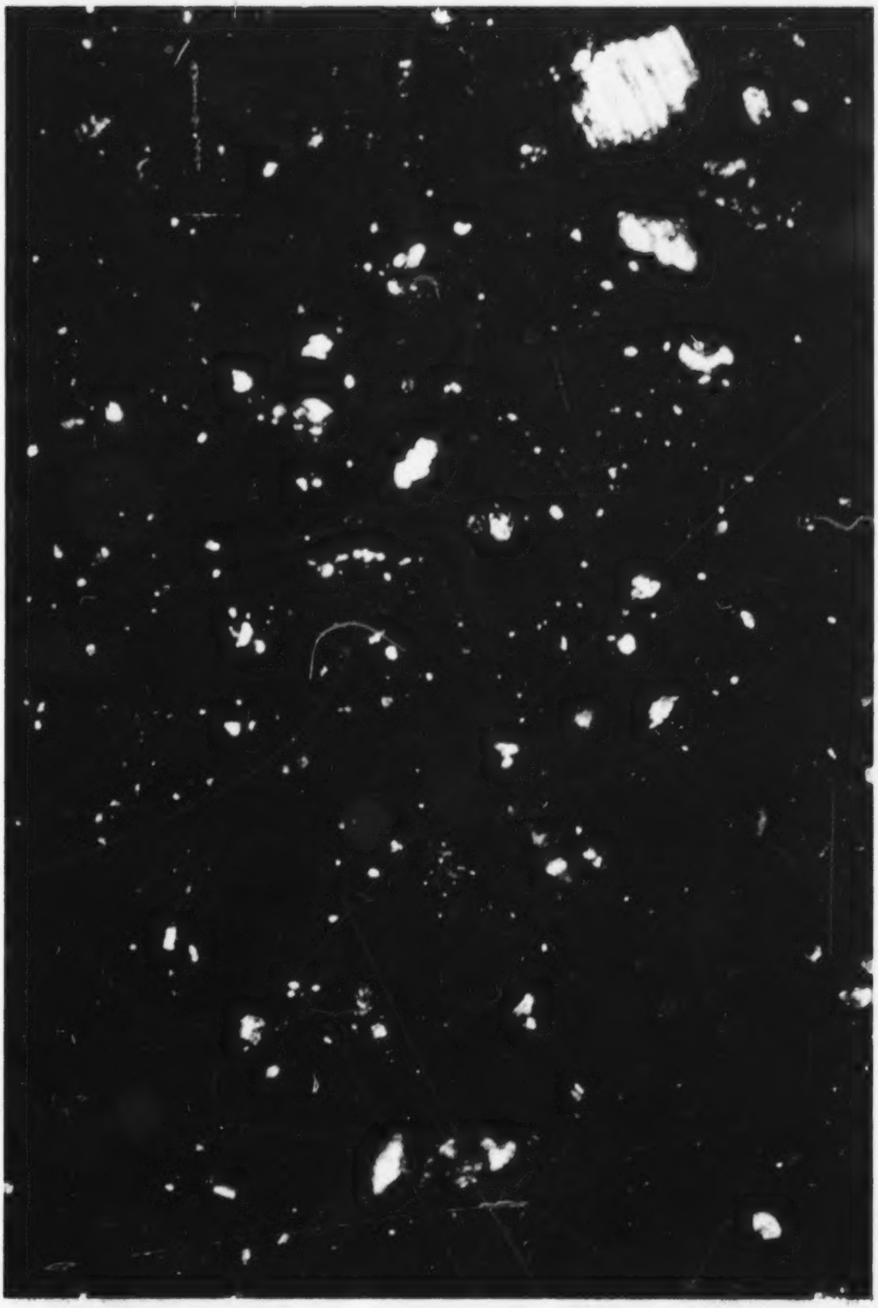


Figure C-14 - 135-6 Showing Limestone; PUP, 51X

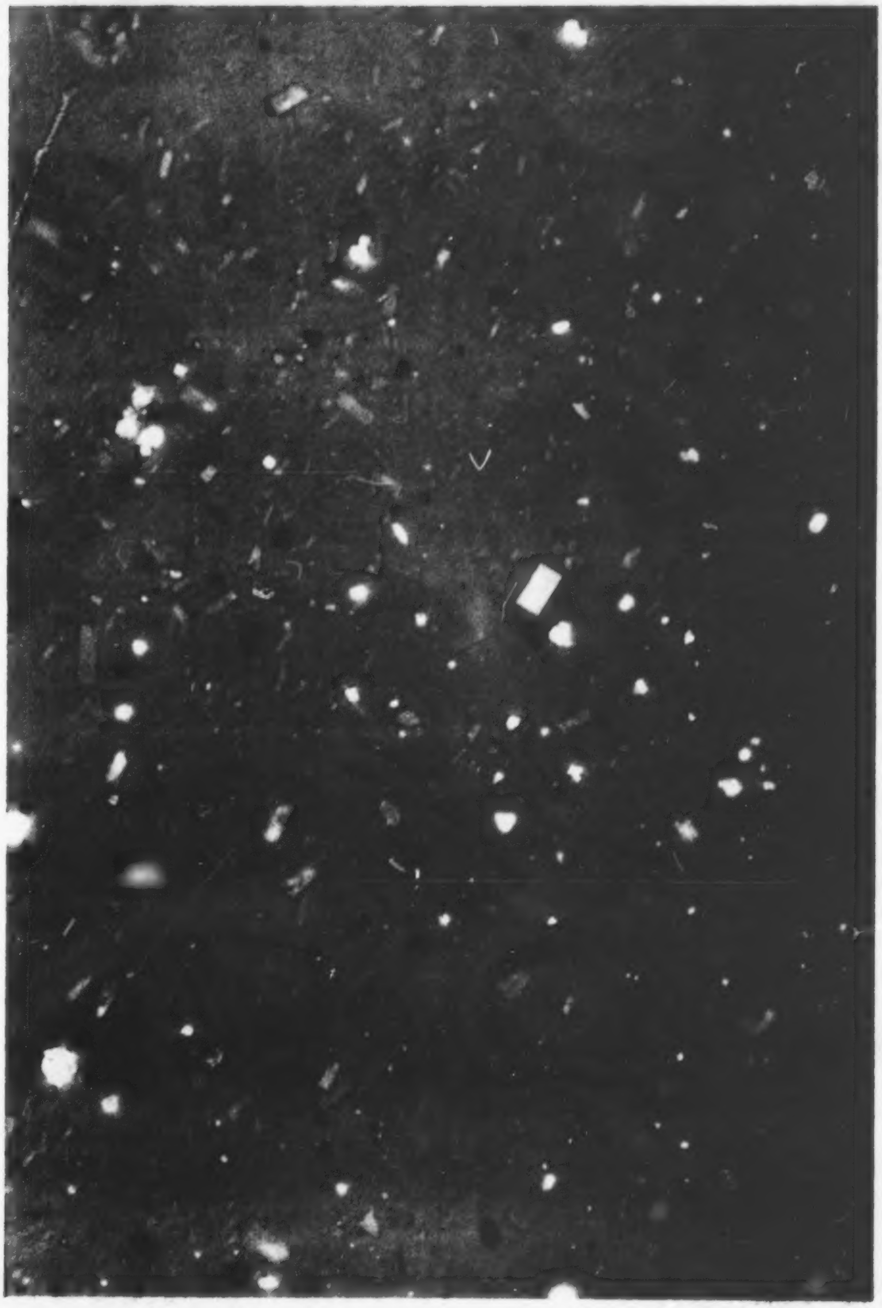


Figure C-15 - 135-7 Showing General View of This Sample at Low Magnification: PUP 51X.

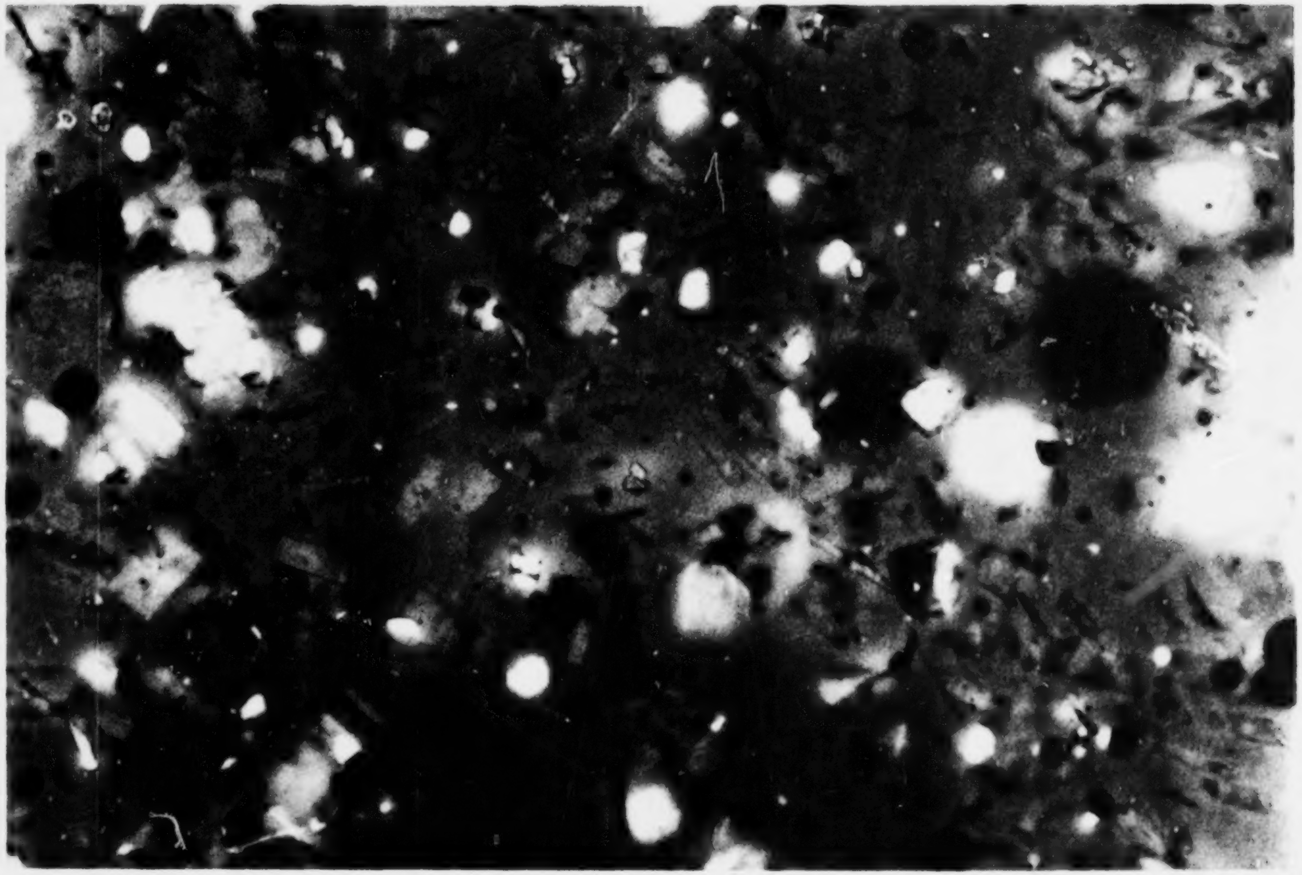


Figure C-16 - 135-7 Showing $CaSO_3 \cdot 1/2H_2O$ Laths, Limestone, Flyash, and Magnetite; PUP, 131X.

The limestone is present both as single crystals and as aggregates of smaller crystals. They range in size from <1μm up to 200μm in diameter (average diameter: 9μm) and the thickness is generally on the same order of magnitude as the diameter. This means that the limestone particles are quite massive compared with the $CaSO_3 \cdot 1/2\ H_2O$ laths.

Magnetite and glassy flyash are each 5-10% of the sample mass. The flyash ranges from clear to dark brown in color. Some flyash spheres are red but most are golden. They range in size from 1-40μm in diameter. The 40μm flyash spheres contain air bubbles and many have non-uniform coloration. A small percentage of the flyash is plerospheres. Magnetite spheres are generally quite large with a modal diameter of about 20μm. No magnetite spheres less than 5μm or greater than 80μm in diameter was seen.

A trace component is partially combusted coal. The coal fragments are present in irregular shapes and with random sizes. The largest fragment of partially combusted coal seen was about 150μm in diameter and it was quite "eaten away" and full of holes.

135-OUT-CYC-Cyclone Catch

Components	Concentration	Average Diameter (μm)	Size Range (μm)
Flyash	15-30%	2	<1-40
Partially combusted coal	<2%	2	<1-80
Crystallized minerals:			
Type 2	70-85%		

This sample was received very wet, with the consistency of a slurry rather than that of a powder. To prepare it for analysis, the sample was spread on to a slide and desiccated for a few days. It was then mounted in a 1.515 refractive index oil.

70-85% of this sample is composed of a crystalline crust (Type 2) which formed when the sample was dried (Figure C-17). The particulates collected in this sample are held in this crust. Figures C-18 and C-19 show the crystalline material at high magnification in the SEM.

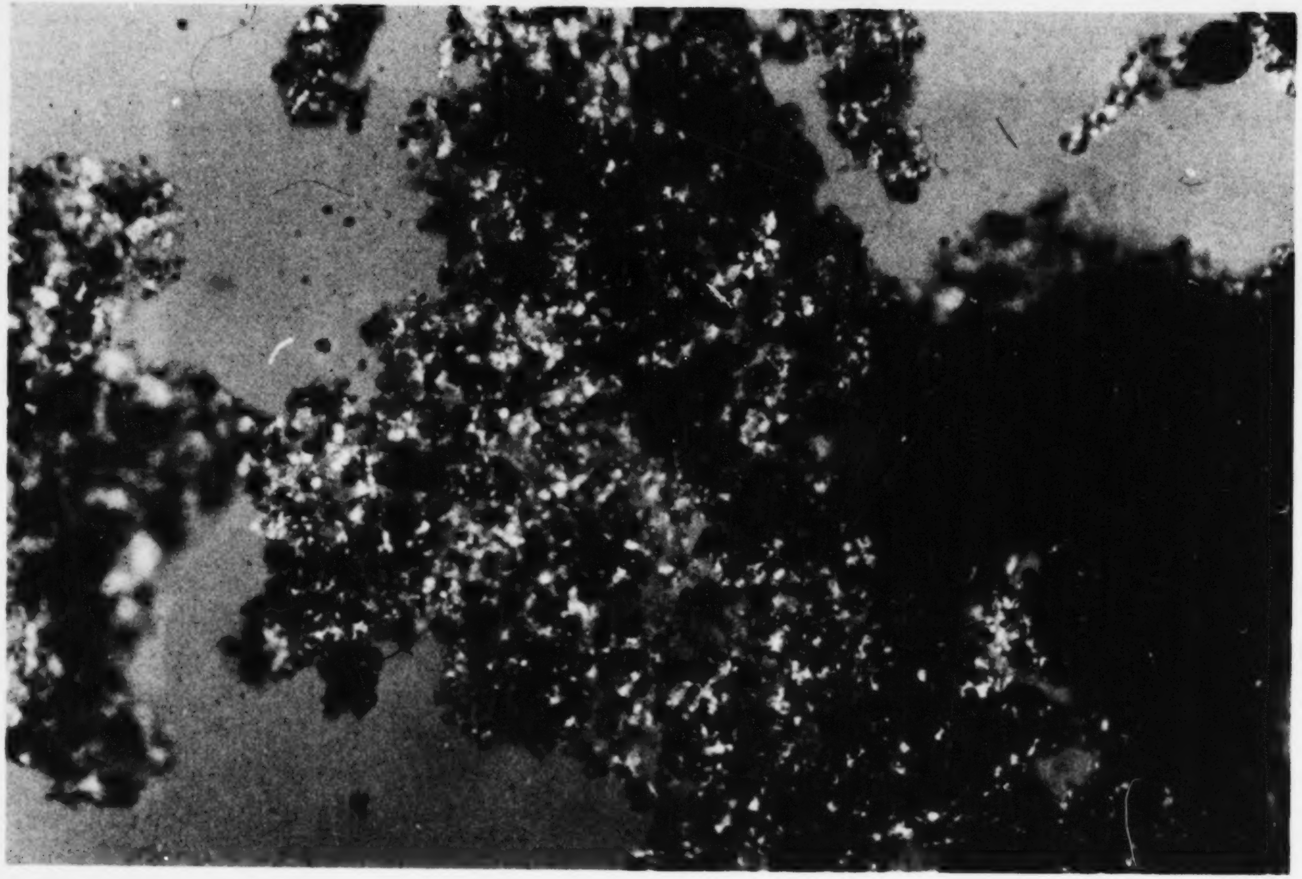


Figure C-17 - 135-OUT-CYC Showing Type 2 Crystallized "Crust" With Flyash Embedded in it: PUP, 51X.

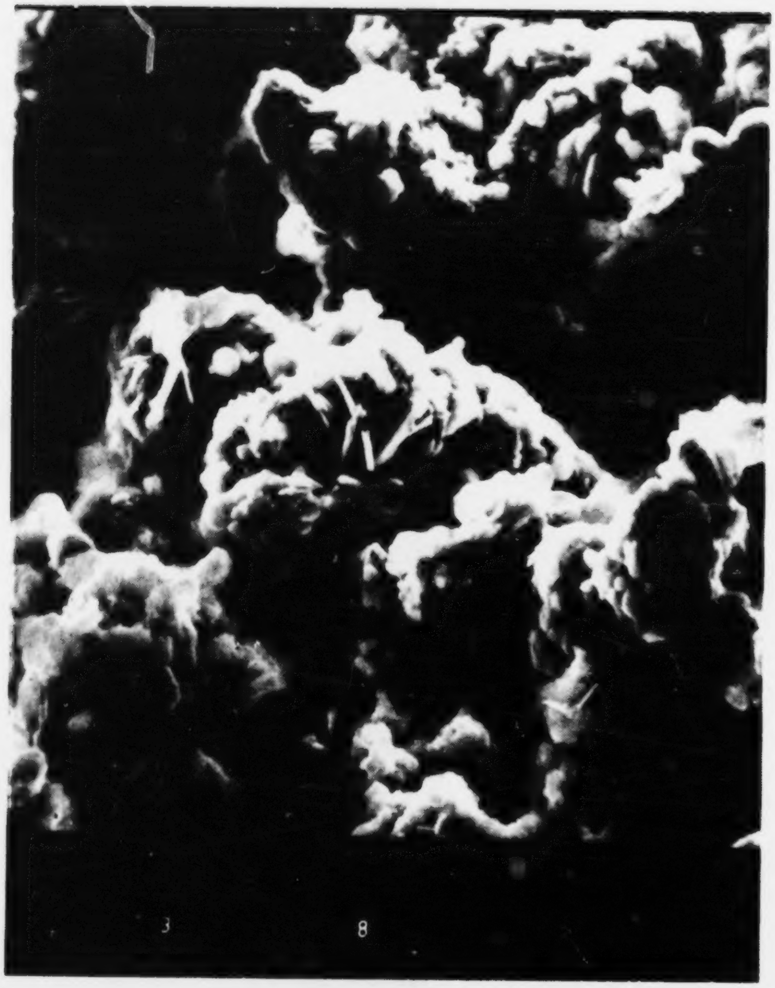


Figure C-18 - SEM Photograph of 135-OUT-CYC Showing Flyash and Crystalline Material Aggregates

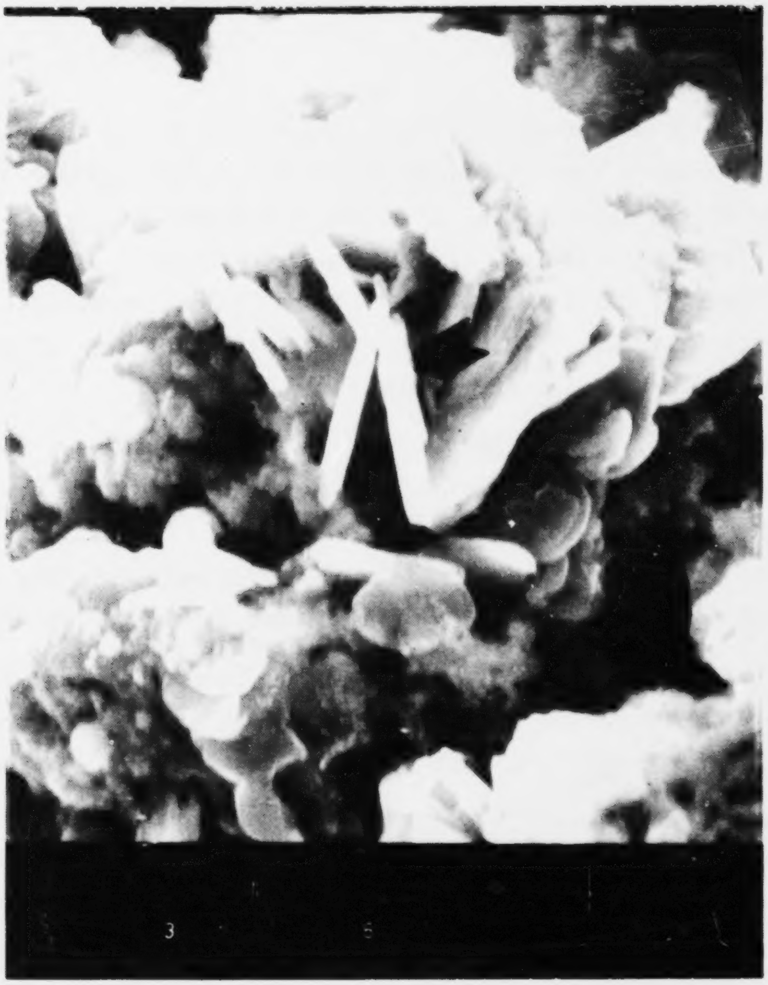


Figure C-19 - SEM-EDX (2000X) Photograph of Crystalline Material in 135-OUT-CYC. EDX Analysis: High Fe & S; Low Si, Zn, Ca

Flyash is 15-30% of this sample. There are some flyash spheres which are 40μm in diameter though the average size is only about 2μm. As in most samples, the flyash spheres are predominantly golden brown and a small percentage are plerospheres.

Partially combusted coal accounts for less than 2% of the sample mass. The average diameter is about 2μm and the diameters of these irregular chunks range from <1μm-80μm.

135-OUT-PF, 135-OUT-PFa

These samples are composed almost exclusively of the three crystallized materials which were described in the general discussion of samples. In both samples, all three types of minerals are present in almost equal quantities, though the spherulitic form may contribute a slightly greater mass than either of the other 2 types (Figure C-20). The nodules in 135-OUT have a average diameter of about 24μm whereas those on the 135-OUT-PFa sample have an average diameter closer to 16μm.

On closer study with an SEM the nodules appear to have a curious donut shape (Figure C-21). At higher resolution (5500X) the crystalline nature of the nodule is clearly seen, (Figure C-22). In addition to the donut nodules, cubic crystals and their platelike materials are also seen (Figure C-23). The donut shaped particles were only found in PFa.

These samples are extremely hygroscopic. Droplets, perhaps 1mm in diameter were formed on the filters when received. The samples were desiccated before mounting so that little of the droplets remained.

The nodules were found in the samples immediately upon mounting before desiccation and remained unaltered after desiccation. The other two types formed during desiccation.

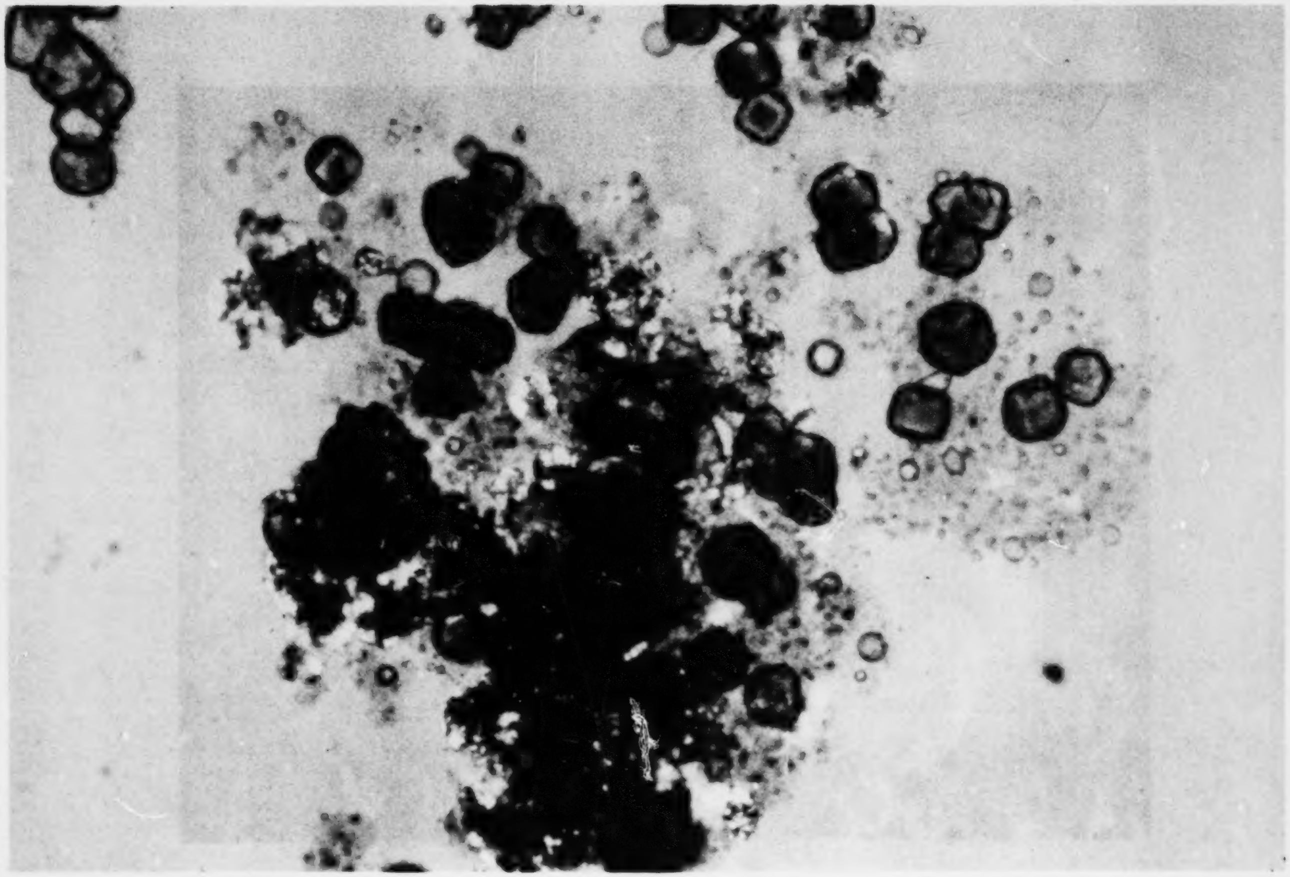


Figure C-20 - 135-OUT-PF Showing the Crystal Types Present in This and the 135-OUT-PFa Samples; PUP, 51X.

Figure C-21 - SEM of 135-OUT-PFa Filter (500X)
Showing Donut-Shaped Particles

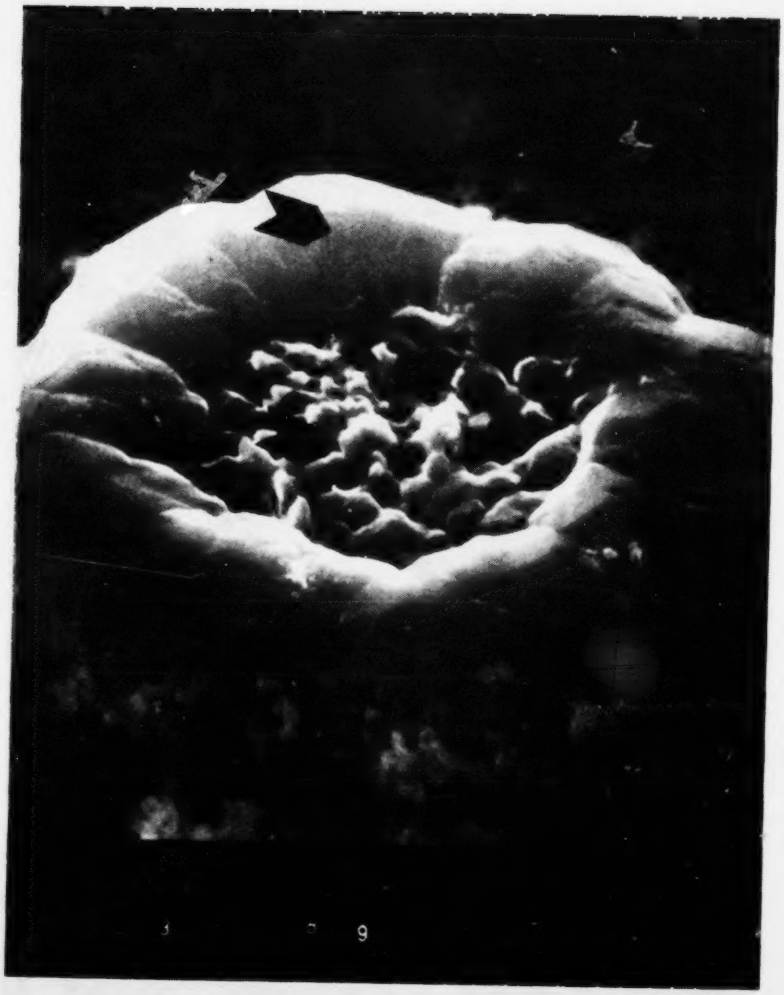


Figure C-22 - SEM-EDX Enlargement (5500X) of Single Nodule from 135-OUT-PFa. Arrow 1 EDX: High S, Fe, Zn; Low Ca, Si, K. Arrow 2 EDX: High S, Fe, Zn; Medium Si; Low K, Ca

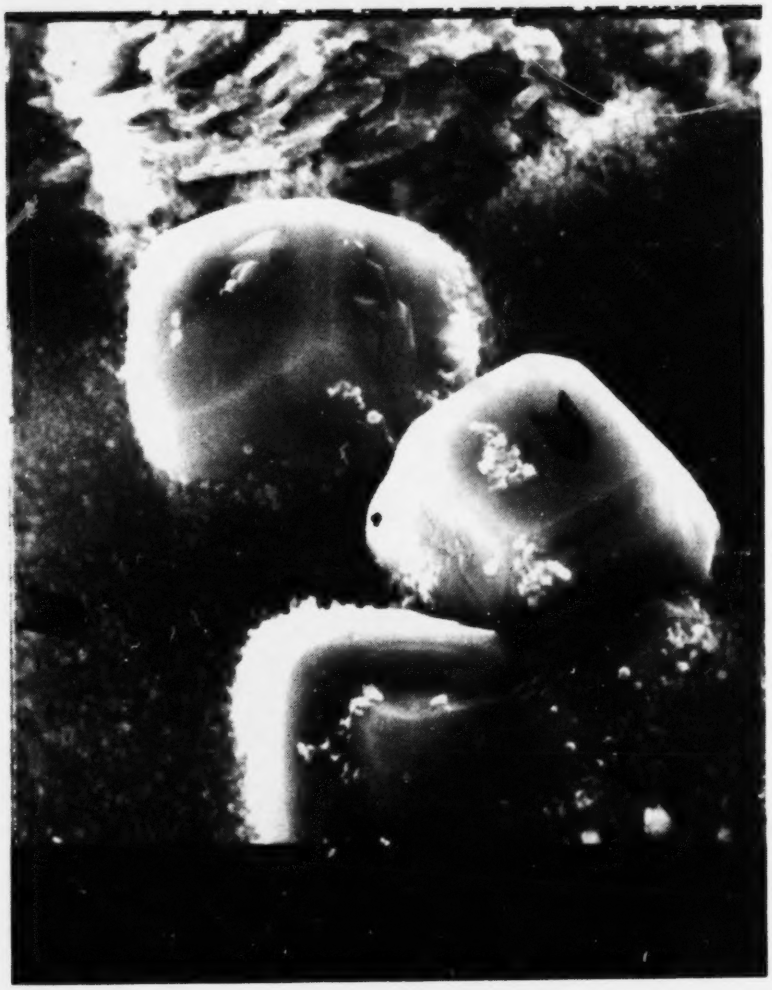


Figure C-23 - SEM-EDX of 135-OUT-PF Showing Cubic and Platelet Materials. Arrow 1 EDX: High S, Fe, Zn; Low K. Arrow 2 EDX: High Fe, Si, Ca, Zn, S

SSMS

Trace element analyses by SSMS of the following coal firing samples are presented in Tables C-4 to C-20:

- Coal Feed (tests 132-136)
- Combined Flue Gas Particulates (test 135)
- Boiler Feedwater (test 132)
- Demister Inlet (test 132)
- Settling Pond Overflow (test 132)
- Inlet Scrubber Water (test 132)
- Water to Slag Pond (test 132)
- Lime Feed (test 135)
- Inlet Scrubber Slurry Liquid (test 135)
- Inlet Scrubber Slurry Solids (test 135)
- Outlet Scrubber Slurry Liquid (test 135)
- Outlet Scrubber Slurry Solids (test 135)
- Bottom Ash (test 133)

XRD

All samples, powders and filters, were analyzed on the Diano-8000 x-ray diffractometer with $Cu_{K\alpha}$ radiation. Instrument parameters were constant for all samples. Powder samples were ground to ca 40μ size and then packed in a sample holder. Filter samples were pressed to ensure a smooth surface and were mounted on a flat surface with double-back Scotch tape. A filter blank was run. No diffraction pattern was observed. Thus, the glass fiber filters did not interfere in the analysis of filter samples.

Results of these analyses are summarized in Table C-21. Standard ASTM d-spacings were used for matching compounds.

MRI Impactor Data

PLM analysis was performed on the inlet particulates for test 135. MRI impactor data were gathered for tests 135 and 136 at the outlet. The impactor data was reduced using the procedure developed by Ensor (Reference C-1). In this approach the data is normalized so that a smooth curve can be drawn through the limited number of data points obtained from the impactor. In order to draw a smooth curve, the geometric mean of the D_{50}'s*

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* The D_{50} of an impactor stage is the calculated aerodynamic particle diameter for which the stage achieves 50% efficiency: one half of the particles of that diameter are captured and one half are not.

TABLE C-4. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF COAL FEED - TEST 132 (132-CF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	14	Terbium	0.4	Ruthenium		Vanadium	90
Thorium	10	Gadolinium	1	Molybdenum	20	Titanium	MC
Bismuth	≤0.2	Europium	0.5	Niobium	9	Scandium	5
Lead	*360	Samarium	4	Zirconium	160	Calcium	MC
Thallium	≤1	Neodymium	10	Yttrium	29	Potassium	MC
Mercury	NR	Praseodymium	5	Strontium	140	Chlorine	13
Gold		Cerium	52	Rubidium	77	Sulfur	MC
Platinum		Lanthanum	41	Bromine	2	Phosphorus	150
Iridium		Barium	320	Selenium	11	Silicon	MC
Osmium		Cesium	5	Arsenic	62	Aluminum	MC
Rhenium		Iodine	4	Germanium	4	Magnesium	MC
Tungsten	≤0.9	Tellurium	≤0.3	Gallium	13	Sodium	MC
Tantalum		Antimony	14	Zinc	59	Fluorine	≈780
Hafnium	2	Tin	2	Copper	96	Oxygen	NR
Lutetium	0.2	Indium	STD	Nickel	37	Nitrogen	NR
Ytterbium	0.9	Cadmium	0.7	Cobalt	17	Carbon	NR
Thulium	0.1	Silver	2	Iron	MC	Boron	21
Erbium	0.8	Palladium		Manganese	300	Beryllium	0.7
Holmium	1	Rhodium		Chromium	100	Lithium	6
Dysprosium	2					Hydrogen	NR

NR – Not Reported
All elements not reported <0.1 ppm weight
MC – Major Component

*Heterogeneous

TABLE C-5. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF COAL FEED - TEST 133 (133-CF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	17	Terbium	0.6	Ruthenium		Vanadium	47
Thorium	12	Gadolinium	2	Molybdenum	32	Titanium	MC
Bismuth	≤0.2	Europium	0.8	Niobium	7	Scandium	8
Lead	340	Samarium	7	Zirconium	91	Calcium	MC
Thallium	≤2	Neodymium	10	Yttrium	21	Potassium	MC
Mercury	NR	Praseodymium	7	Strontium	180	Chlorine	20
Gold		Cerium	55	Rubidium	81	Sulfur	MC
Platinum		Lanthanum	37	Bromine	2	Phosphorus	970
Iridium		Barium	380	Selenium	43	Silicon	MC
Osmium		Cesium	5	Arsenic	39	Aluminum	MC
Rhenium		Iodine	3	Germanium	6	Magnesium	MC
Tungsten	≤0.8	Tellurium	≤0.5	Gallium	16	Sodium	MC
Tantalum		Antimony	11	Zinc	185	Fluorine	≈390
Hafnium	1	Tin	1	Copper	84	Oxygen	NR
Lutetium	0.3	Indium	STD	Nickel	10	Nitrogen	NR
Ytterbium	1	Cadmium	1	Cobalt	14	Carbon	NR
Thulium	0.2	Silver	2	Iron	MC	Boron	59
Erbium	1	Palladium		Manganese	57	Beryllium	1
Holmium	2	Rhodium		Chromium	54	Lithium	49
Dysprosium	3					Hydrogen	NR

NR – Not Reported
All elements not reported <0.2 ppm weight
MC – Major Component

TABLE C-6. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF COAL FEED - TEST 134 (134-CF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	*63	Terbium	0.4	Ruthenium		Vanadium	45
Thorium	13	Gadolinium	1	Molybdenum	13	Titanium	MC
Bismuth	≤0.1	Europium	0.7	Niobium	6	Scandium	2
Lead	200	Samarium	4	Zirconium	73	Calcium	MC
Thallium	≤0.2	Neodymium	10	Yttrium	*120	Potassium	MC
Mercury	NR	Praseodymium	6	Strontium	180	Chlorine	17
Gold		Cerium	66	Rubidium	39	Sulfur	MC
Platinum		Lanthanum	120	Bromine	2	Phosphorus	170
Iridium		Barium	480	Selenium	55	Silicon	MC
Osmium		Cesium	5	Arsenic	31	Aluminum	MC
Rhenium	≤0.2	Iodine	3	Germanium	10	Magnesium	MC
Tungsten	≤2	Tellurium	≤0.3	Gallium	33	Sodium	MC
Tantalum		Antimony	16	Zinc	130	Fluorine	=39
Hafnium	1	Tin	2	Copper	60	Oxygen	NR
Lutetium	0.2	Indium	STD	Nickel	15	Nitrogen	NR
Ytterbium	1	Cadmium	0.8	Cobalt	11	Carbon	NR
Thulium	0.1	Silver	4	Iron	MC	Boron	17
Erbium	0.8	Palladium		Manganese	57	Beryllium	0.6
Holmium	1	Rhodium		Chromium	34	Lithium	6
Dysprosium	2					Hydrogen	NR

NR – Not Reported
All elements not-reported <0.1 ppm weight
MC – Major Component *Heterogeneous

TABLE C-7. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF COAL FEED - TEST 135 (135-CF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	46	Terbium	0.3	Ruthenium		Vanadium	33
Thorium	31	Gadolinium	0.8	Molybdenum	16	Titanium	MC
Bismuth	≤0.1	Europium	0.4	Niobium	7	Scandium	2
Lead	470	Samarium	5	Zirconium	47	Calcium	MC
Thallium	0.3	Neodymium	9	Yttrium	14	Potassium	MC
Mercury	NR	Praseodymium	7	Strontium	100	Chlorine	18
Gold		Cerium	38	Rubidium	70	Sulfur	MC
Platinum		Lanthanum	34	Bromine	1	Phosphorus	140
Iridium		Barium	770	Selenium	10	Silicon	MC
Osmium		Cesium	4	Arsenic	68	Aluminum	MC
Rhenium		Iodine	3	Germanium	16	Magnesium	MC
Tungsten	0.7	Tellurium	≤0.1	Gallium	5	Sodium	MC
Tantalum		Antimony	6	Zinc	95	Fluorine	≈76
Hafnium	0.8	Tin	1	Copper	19	Oxygen	NR
Lutetium	0.2	Indium	STD	Nickel	18	Nitrogen	NR
Ytterbium	0.8	Cadmium	0.5	Cobalt	10	Carbon	NR
Thulium	0.1	Silver	0.5	Iron	MC	Boron	14
Erbium	0.6	Palladium		Manganese	110	Beryllium	0.2
Holmium	0.8	Rhodium		Chromium	25	Lithium	3
Dysprosium	1					Hydrogen	NR

NR – Not Reported
All elements not-reported <0.1 ppm weight
MC – Major Component

TABLE C-8. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF COAL FEED - TEST 136 (136-CF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	22	Terbium	0.8	Ruthenium		Vanadium	69
Thorium	16	Gadolinium	2	Molybdenum	41	Titanium	MC
Bismuth	≤0.2	Europium	1	Niobium	11	Scandium	2
Lead	170	Samarium	5	Zirconium	48	Calcium	MC
Thallium	≤1	Neodymium	10	Yttrium	30	Potassium	MC
Mercury	NR	Praseodymium	11	Strontium	150	Chlorine	52
Gold		Cerium	36	Rubidium	35	Sulfur	MC
Platinum		Lanthanum	42	Bromine	3	Phosphorus	160
Iridium		Barium	440	Selenium	45	Silicon	MC
Osmium		Cesium	5	Arsenic	38	Aluminum	MC
Rhenium		Iodine	11	Germanium	9	Magnesium	MC
Tungsten	2	Tellurium		Gallium	14	Sodium	MC
Tantalum		Antimony	29	Zinc	*150	Fluorine	=130
Hafnium	2	Tin	2	Copper	55	Oxygen	NR
Lutetium	0.2	Indium	STD	Nickel	38	Nitrogen	NR
Ytterbium	1	Cadmium	*3	Cobalt	18	Carbon	NR
Thulium	0.1	Silver	2	Iron	MC	Boron	22
Erbium	0.2	Palladium		Manganese	310	Beryllium	1
Holmium	1	Rhodium		Chromium	35	Lithium	6
Dysprosium	2					Hydrogen	NR

NR – Not Reported
All elements not reported <0.1 ppm weight
MC – Major Component
*Heterogeneous

TABLE C-9. COMBINED SPARK SOURCE MASS SPECTROMETRY ANALYSES OF FLUE GAS PARTICULATES - TEST 135

Element	Concentration, mg/m^3	
	Inlet	Outlet
Al	1.94	> 0.139
Ag	> 20.6	0.036
As	> 95.1	> 9.00
B	0.300	0.039
Ba	> 2.34	0.320
Be	0.0034	0.001
Bi	0.012	0.002
Ca	179.6	>44.0
Cd	0.862	0.316
Ce	0.688	0.011
Cl	> 0.524	0.206
Co	0.088	0.007
Cr	0.975	>26.0
Cs	0.106	0.003
Cu	1.958	>26.0
F	0.27	0.062
Fe	>134.9	>62.6
Ga	0.889	0.020
Ge	0.415	0.070
K	>101.0	10.4
La	0.670	0.003
Li	0.108	0.011
Mg	> 49.0	> 0.122
Mn	> 1.62	0.02
Mo	0.994	0.155
Na	> 49.0	> 0.372
Nb	0.233	0.004
Nd	0.136	0.001
Ni	> 1.03	0.036
P	>100.8	62.6
Pb	>100.4	>90.0
Rb	0.557	0.007
Sb	0.888	0.117
Se	0.376	0.130
Si	> 1.92	41.0
Sn	0.160	0.025
Sr	> 1.658	0.047
Ti	>100.4	> 9.00
Tl	0.192	0.043
U	> 0.786	0.09
V	1.008	0.128
Y	0.262	0.004
Zn	>134.9	>76.00
Zr	0.833	0.005

TABLE C-10. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF BOILER FEEDWATER - TEST 132 (132-6-1-1)

CONCENTRATION IN μg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.07	Terbium		Ruthenium		Vanadium	0.03
Thorium	0.4	Gadolinium		Molybdenum	0.09	Titanium	0.2
Bismuth	0.03	Europium		Niobium		Scandium	≤0.002
Lead	0.09	Samarium		Zirconium	0.01	Calcium	3
Thallium		Neodymium		Yttrium		Potassium	0.2
Mercury	NR	Praseodymium		Strontium	0.03	Chlorine	0.1
Gold		Cerium	0.005	Rubidium	0.002	Sulfur	1
Platinum		Lanthanum	0.005	Bromine	0.008	Phosphorus	0.03
Iridium		Barium	0.2	Selenium	0.05	Silicon	0.3
Osmium		Cesium		Arsenic	0.09	Aluminum	0.04
Rhenium		Iodine	0.009	Germanium		Magnesium	0.09
Tungsten	≤0.02	Tellurium	≤0.04	Gallium	0.001	Sodium	0.03
Tantalum		Antimony	0.1	Zinc	0.1	Fluorine	=0.03
Hafnium		Tin	0.008	Copper	0.1	Oxygen	NR
Lutetium		Indium	STD	Nickel	0.02	Nitrogen	NR
Ytterbium		Cadmium		Cobalt	0.003	Carbon	NR
Thulium		Silver	0.008	Iron	0.5	Boron	0.001
Erbium		Palladium		Manganese	0.01	Beryllium	
Holmium		Rhodium		Chromium	0.05	Lithium	<0.001
Dysprosium						Hydrogen	NR

NR – Not Reported
All elements not reported < 0.002 μg/ml
MC – Major Component

TABLE C-11. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF DEMISTER INLET - TEST 132 (132-6-2-1)

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.04	Terbium		Ruthenium		Vanadium	0.004
Thorium		Gadolinium		Molybdenum	0.5	Titanium	0.04
Bismuth		Europium		Niobium	0.005	Scandium	≤0.001
Lead	0.01	Samarium		Zirconium	0.008	Calcium	MC
Thallium		Neodymium		Yttrium	0.004	Potassium	MC
Mercury	NR	Praseodymium	0.001	Strontium	3	Chlorine	1
Gold		Cerium	0.003	Rubidium	0.02	Sulfur	>8
Platinum		Lanthanum	0.003	Bromine	0.9	Phosphorus	0.09
Iridium		Barium	0.5	Selenium	0.1	Silicon	1
Osmium		Cesium		Arsenic	0.05	Aluminum	0.04
Rhenium	≤0.005	Iodine	0.3	Germanium	0.01	Magnesium	MC
Tungsten		Tellurium	≤0.004	Gallium	0.002	Sodium	>3
Tantalum		Antimony	0.01	Zinc	0.5	Fluorine	≈0.4
Hafnium		Tin		Copper	0.1	Oxygen	NR
Lutetium		Indium	STD	Nickel	0.07	Nitrogen	NR
Ytterbium		Cadmium	0.009	Cobalt	0.01	Carbon	NR
Thulium		Silver	0.001	Iron	0.3	Boron	2
Erbium		Palladium		Manganese	0.6	Beryllium	
Holmium		Rhodium		Chromium	≤0.03	Lithium	0.02
Dysprosium						Hydrogen	NR

NR – Not Reported

All elements not reported <0.001 µg/ml

MC – Major Component

TABLE C-12. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF SETTLING POND OVERFLOW - TEST 132 (132-6-3-1)

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.02	Terbium		Ruthenium		Vanadium	0.002
Thorium		Gadolinium		Molybdenum	0.3	Titanium	≤0.008
Bismuth		Europium	<0.001	Niobium	0.003	Scandium	<0.001
Lead	0.06	Samarium	0.002	Zirconium	0.003	Calcium	MC
Thallium	≤0.002	Neodymium	<0.001	Yttrium	0.001	Potassium	>4
Mercury	NR	Praseodymium	<0.001	Strontium	4	Chlorine	MC
Gold		Cerium	0.004	Rubidium	0.02	Sulfur	>2
Platinum		Lanthanum	0.003	Bromine	0.6	Phosphorus	0.04
Iridium		Barium	0.2	Selenium	0.1	Silicon	0.5
Osmium		Cesium	<0.001	Arsenic	0.5	Aluminum	0.1
Rhenium	0.004	Iodine	0.2	Germanium	0.02	Magnesium	MC
Tungsten	0.003	Tellurium	≤0.002	Gallium	0.001	Sodium	>1
Tantalum		Antimony	0.02	Zinc	5	Fluorine	=0.5
Hafnium		Tin	0.001	Copper	0.01	Oxygen	NR
Lutetium		Indium	STD	Nickel	INT	Nitrogen	NR
Ytterbium		Cadmium	0.02	Cobalt	0.01	Carbon	NR
Thulium		Silver	0.001	Iron	0.3	Boron	≥6
Erbium		Palladium		Manganese	>3	Beryllium	<0.001
Holmium		Rhodium		Chromium	0.02	Lithium	0.02
Dysprosium						Hydrogen	NR

NR – Not Reported
All elements not reported <0.001 µg/ml.
MC – Major Component INT-Interference

TABLE C-13. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF INLET SCRUBBER WATER - TEST 132 (132-6-4-1)

CONCENTRATION IN μg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.01	Terbium		Ruthenium		Vanadium	0.004
Thorium		Gadolinium		Molybdenum	0.6	Titanium	0.4
Bismuth		Europium		Niobium	0.003	Scandium	<0.001
Lead	0.01	Samarium		Zirconium	0.009	Calcium	MC
Thallium		Neodymium	0.002	Yttrium	0.003	Potassium	>8
Mercury	NR	Praseodymium	<0.001	Strontium	2	Chlorine	3
Gold		Cerium	0.002	Rubidium	0.02	Sulfur	>4
Platinum		Lanthanum	0.003	Bromine	0.2	Phosphorus	0.05
Iridium		Barium	0.2	Selenium	0.08	Silicon	2
Osmium		Cesium	0.001	Arsenic	0.06	Aluminum	0.03
Rhenium	≤0.004	Iodine	0.3	Germanium	≤0.01	Magnesium	MC
Tungsten		Tellurium	≤0.002	Gallium	0.001	Sodium	>2
Tantalum		Antimony	0.02	Zinc	0.6	Fluorine	≈2
Hafnium		Tin	0.002	Copper	0.009	Oxygen	NR
Lutetium		Indium	STD	Nickel	0.07	Nitrogen	NR
Ytterbium		Cadmium	0.005	Cobalt	0.01	Carbon	NR
Thulium		Silver	0.001	Iron	0.3	Boron	1
Erbium		Palladium		Manganese	1	Beryllium	
Holmium		Rhodium		Chromium	0.08	Lithium	0.02
Dysprosium						Hydrogen	NR

NR – Not Reported
All elements not reported < 0.001 μg/ml
MC – Major Component

TABLE C-14. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF WATER TO SLAG POND - TEST 132 (132-6-5-1)

CONCENTRATION IN μg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.05	Terbium		Ruthenium		Vanadium	0.01
Thorium		Gadolinium		Molybdenum	0.1	Titanium	0.06
Bismuth	0.2	Europium		Niobium	0.004	Scandium	≤0.002
Lead	0.09	Samarium		Zirconium	0.005	Calcium	MC
Thallium		Neodymium		Yttrium		Potassium	MC
Mercury	NR	Praseodymium		Strontium	2	Chlorine	9
Gold		Cerium	0.009	Rubidium	0.004	Sulfur	MC
Platinum		Lanthanum	0.009	Bromine	0.4	Phosphorus	0.1
Iridium		Barium	1	Selenium	0.01	Silicon	0.7
Osmium		Cesium		Arsenic	0.04	Aluminum	>2
Rhenium		Iodine	0.4	Germanium		Magnesium	7
Tungsten		Tellurium	0.006	Gallium	0.003	Sodium	>5
Tantalum		Antimony		Zinc	0.5	Fluorine	=0.3
Hafnium		Tin		Copper	0.05	Oxygen	NR
Lutetium		Indium	STD	Nickel	0.08	Nitrogen	NR
Ytterbium		Cadmium	0.006	Cobalt	≤0.003	Carbon	NR
Thulium		Silver		Iron	1	Boron	0.4
Erbium		Palladium		Manganese	0.08	Beryllium	
Holmium		Rhodium		Chromium	0.1	Lithium	0.007
Dysprosium						Hydrogen	NR

NR – Not Reported
All elements not reported <0.002 μg/ml
MC – Major Component

TABLE C-15. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF LIME FEED - TEST 135 (135-LF)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	18	Terbium	0.4	Ruthenium		Vanadium	30
Thorium	10	Gadolinium	1	Molybdenum	6	Titanium	800
Bismuth	0.3	Europium	0.7	Niobium	5	Scandium	0.7
Lead	20	Samarium	5	Zirconium	65	Calcium	MC
Thallium	≤0.2	Neodymium	5	Yttrium	7	Potassium	MC
Mercury	NR	Praseodymium	5	Strontium	MC	Chlorine	13
Gold		Cerium	30	Rubidium	20	Sulfur	MC
Platinum		Lanthanum	23	Bromine	0.9	Phosphorus	870
Iridium		Barium	220	Selenium	0.6	Silicon	MC
Osmium		Cesium	1	Arsenic	5	Aluminum	MC
Rhenium		Iodine	11	Germanium	0.3	Magnesium	MC
Tungsten	0.7	Tellurium	≤0.4	Gallium	4	Sodium	NR
Tantalum	≤0.3	Antimony	1	Zinc	15	Fluorine	=180
Hafnium	0.3	Tin	1	Copper	15	Oxygen	NR
Lutetium	<0.1	Indium	STD	Nickel	9	Nitrogen	NR
Ytterbium	0.5	Cadmium	1	Cobalt	1	Carbon	NR
Thulium	<0.1	Silver	0.3	Iron	MC	Boron	3
Erbium	0.5	Palladium		Manganese	≥520	Beryllium	0.2
Holmium	0.6	Rhodium		Chromium	19	Lithium	7
Dysprosium	1					Hydrogen	NR

NR – Not Reported
All elements not reported <0.1 ppm weight
MC – Major Component

TABLE C-16. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF INLET SCRUBBER SLURRY LIQUID - TEST 135 (135-6-LIQUID)

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.1	Terbium		Ruthenium		Vanadium	0.008
Thorium		Gadolinium		Molybdenum	1	Titanium	≤0.03
Bismuth		Europium		Niobium	0.01	Scandium	≤0.002
Lead	0.02	Samarium		Zirconium	0.02	Calcium	MC
Thallium		Neodymium		Yttrium	≤0.009	Potassium	MC
Mercury	NR	Praseodymium		Strontium	8	Chlorine	MC
Gold		Cerium	0.008	Rubidium	0.02	Sulfur	>8
Platinum		Lanthanum	0.01	Bromine	1	Phosphorus	0.1
Iridium		Barium	0.1	Selenium	0.07	Silicon	1
Osmium		Cesium	<0.001	Arsenic	3	Aluminum	0.02
Rhenium		Iodine	0.2	Germanium	0.03	Magnesium	MC
Tungsten	≤0.03	Tellurium	≤0.01	Gallium	0.02	Sodium	>3
Tantalum		Antimony	0.03	Zinc	0.3	Fluorine	MC
Hafnium		Tin	0.005	Copper	0.05	Oxygen	NR
Lutetium		Indium	STD	Nickel	INT	Nitrogen	NR
Ytterbium		Cadmium	0.01	Cobalt	0.02	Carbon	NR
Thulium		Silver	0.002	Iron	0.1	Boron	8
Erbium		Palladium		Manganese	0.04	Beryllium	
Holmium		Rhodium		Chromium	0.04	Lithium	<0.1
Dysprosium						Hydrogen	NR

NR — Not Reported

All elements not reported <0.002 µg/ml

MC — Major Component INT-Interference

TABLE C-17. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF INLET SCRUBBER SLURRY SOLIDS - TEST 135 (135-6-SOLID)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	11	Terbium	0.6	Ruthenium		Vanadium	13
Thorium	7	Gadolinium	2	Molybdenum	15	Titanium	200
Bismuth		Europium	0.8	Niobium	3	Scandium	0.2
Lead	12	Samarium	4	Zirconium	29	Calcium	MC
Thallium		Neodymium	2	Yttrium	10	Potassium	MC
Mercury	NR	Praseodymium	4	Strontium	MC	Chlorine	17
Gold		Cerium	40	Rubidium	13	Sulfur	MC
Platinum		Lanthanum	31	Bromine	0.8	Phosphorus	230
Iridium		Barium	320	Selenium	2	Silicon	MC
Osmium		Cesium	4	Arsenic	4	Aluminum	MC
Rhenium		Iodine	7	Germanium	1	Magnesium	MC
Tungsten		Tellurium		Gallium	6	Sodium	MC
Tantalum		Antimony	1	Zinc	45	Fluorine	≈240
Hafnium		Tin	2	Copper	4	Oxygen	NR
Lutetium	<0.1	Indium	STD	Nickel	12	Nitrogen	NR
Ytterbium	0.7	Cadmium	1	Cobalt	1	Carbon	NR
Thulium	0.2	Silver	0.7	Iron	MC	Boron	3
Erbium	0.6	Palladium		Manganese	>690	Beryllium	<0.1
Holmium	0.8	Rhodium		Chromium	19	Lithium	4
Dysprosium	1					Hydrogen	NR

NR – Not Reported

All elements not reported <0.1 ppm weight

MC – Major Component

TABLE C-18. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF OUTLET SCRUBBER SLURRY LIQUID - TEST 135 (135-7-LIQUID)

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	0.01	Terbium		Ruthenium		Vanadium	0.01
Thorium		Gadolinium		Molybdenum	4	Titanium	≤0.02
Bismuth		Europium		Niobium	0.01	Scandium	≤0.001
Lead	≤0.004	Samarium		Zirconium	0.02	Calcium	MC
Thallium		Neodymium		Yttrium	≤0.006	Potassium	MC
Mercury	NR	Praseodymium	0.001	Strontium	6	Chlorine	MC
Gold		Cerium	0.001	Rubidium	0.03	Sulfur	>6
Platinum		Lanthanum	0.009	Bromine	3	Phosphorus	0.06
Iridium		Barium	0.2	Selenium	0.5	Silicon	MC
Osmium		Cesium	<0.001	Arsenic	5	Aluminum	0.004
Rhenium	≤0.01	Iodine	2	Germanium	0.4	Magnesium	MC
Tungsten		Tellurium	≤0.007	Gallium	0.007	Sodium	>3
Tantalum		Antimony	0.07	Zinc	0.06	Fluorine	≈8
Hafnium		Tin	0.003	Copper	0.005	Oxygen	NR
Lutetium		Indium	STD	Nickel	INT	Nitrogen	NR
Ytterbium		Cadmium	0.003	Cobalt	≤0.003	Carbon	NR
Thulium		Silver	0.003	Iron	0.01	Boron	MC
Erbium		Palladium		Manganese	0.5	Beryllium	
Holmium		Rhodium		Chromium	0.2	Lithium	0.1
Dysprosium						Hydrogen	NR

NR – Not Reported
All elements not reported <0.001 µg/ml
MC – Major Component
INT-Interference

TABLE C-19. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF OUTLET SCRUBBER SLURRY SOLIDS - TEST 135 (135-7-SOLID)

CONCENTRATION IN PPM WEIGHT

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	44	Terbium	0.6	Ruthenium		Vanadium	19
Thorium	11	Gadolinium	2	Molybdenum	25	Titanium	880
Bismuth	0.2	Europium	1	Niobium	13	Scandium	2
Lead	820	Samarium	5	Zirconium	73	Calcium	MC
Thallium	6	Neodymium	13	Yttrium	12	Potassium	MC
Mercury	NR	Praseodymium	3	Strontium	910	Chlorine	130
Gold		Cerium	65	Rubidium	22	Sulfur	MC
Platinum		Lanthanum	47	Bromine	5	Phosphorus	970
Iridium		Barium	270	Selenium	7	Silicon	MC
Osmium		Cesium	4	Arsenic	120	Aluminum	MC
Rhenium		Iodine	6	Germanium	17	Magnesium	MC
Tungsten	≤0.3	Tellurium	≤0.4	Gallium	19	Sodium	MC
Tantalum		Antimony	44	Zinc	MC	Fluorine	≈260
Hafnium	0.6	Tin	5	Copper	50	Oxygen	NR
Lutetium	0.3	Indium	STD	Nickel	23	Nitrogen	NR
Ytterbium	1	Cadmium	33	Cobalt	9	Carbon	NR
Thulium	0.2	Silver	3	Iron	MC	Boron	13
Erbium	1	Palladium		Manganese	≥580	Beryllium	0.7
Holmium	2	Rhodium		Chromium	16	Lithium	5
Dysprosium	3					Hydrogen	NR

NR – Not Reported

All elements not reported <0.1 ppm weight

MC – Major Component

TABLE C-20. SPARK SOURCE MASS SPECTROMETRY ANALYSIS OF BOTTOM ASH - TEST 133 (133-18-BA)

CONCENTRATION IN µg/ml

ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.	ELEMENT	CONC.
Uranium	1	Terbium	0.04	Ruthenium		Vanadium	1
Thorium	0.4	Gadolinium	0.1	Molybdenum	0.1	Titanium	MC
Bismuth	MC	Europium	0.1	Niobium	1	Scandium	0.03
Lead	1	Samarium	0.2	Zirconium	2	Calcium	MC
Thallium		Neodymium	1	Yttrium	1	Potassium	>6
Mercury	NR	Praseodymium	0.2	Strontium	3	Chlorine	0.2
Gold		Cerium	2	Rubidium	3	Sulfur	>3
Platinum		Lanthanum	2	Bromine	0.02	Phosphorus	8
Iridium		Barium	MC	Selenium	0.05	Silicon	MC
Osmium		Cesium	0.3	Arsenic	0.03	Aluminum	>1
Rhenium		Iodine	0.004	Germanium	0.03	Magnesium	MC
Tungsten	0.01	Tellurium	≤0.007	Gallium	0.1	Sodium	>1
Tantalum	≤0.001	Antimony	0.04	Zinc	MC	Fluorine	≈0.1
Hafnium	0.03	Tin	0.004	Copper	0.3	Oxygen	NR
Lutetium	0.002	Indium	STD	Nickel	0.8	Nitrogen	NR
Ytterbium	0.04	Cadmium	0.007	Cobalt	0.3	Carbon	NR
Thulium	0.004	Silver	0.005	Iron	MC	Boron	0.1
Erbium	0.04	Palladium		Manganese	>5	Beryllium	0.01
Holmium	0.06	Rhodium		Chromium	0.4	Lithium	0.4
Dysprosium	0.09					Hydrogen	NR

NR – Not Reported
All elements not reported <0.001 µg/ml
MC – Major Component

TABLE C-21. SUMMARY OF XRD ANALYSES OF COAL-FIRED SAMPLES

Sample	Compound Definitely Present	Compounds Possibly Present
135-Out-PF 135-Out-PFa	$CaSO_4$; α-SiO_2; $CaSO_3 \cdot 1/2\ H_2O$	Kaolinite; $Fe_2Al_4Si_5O_{18}$; $Na_2Si_2O_5$; Fe_2SiO_4; barium aluminosilicate
135-In-PF 135-In-PFa	$CaSO_4$	
135-In-CYC	Fe_3O_4	
135-6 135-LF	$CaCO_3$; α-SiO_2	$Li_2B_2O_4 \cdot 16H_2O$; $Ca_5Al_6O_{14}$; $Ba_3Ca_2Ti_2O_9$; $Mg_3Ca(CO_3)_4$
135-7	$CaCO_3$; α-SiO_2; $CaSO_3 \cdot 1/2\ H_2O$	
133-18-BA	Amorphous	
135-PFB	Amorphous, no pattern	

PF, PFa = particle filters, subscript "a" indicates second filter used during run.
CYC = cyclone catch
-6 = inlet scrubber slurry
-7 = outlet scrubber slurry
BA = bottom ash
PFB = blank particle filter
LF = limestone feed

for stages n and n-1 is taken as the average diameter of the particles in stage n. In this case two assumptions were made: (1) the upper limit of the first stage was arbitrarily set at 100μ and (2) the final filter absolute collection point was set at 0.2μ. Figure C-24 shows the differential mass loading at the outlet for tests 135 and 136 plotted against the geometric mean D_{50} for each stage. This method of data presentation allows comparison of mass loadings for the individual impactor stages, which is difficult if the data are presented as cumulative mass loadings. There is good agreement between tests 135 and 136 for outlet loadings on impactor stages 2 to 7. Stage 8 for test 135 showed a weight loss and this data point was discarded. The weight for stage 1 of test 135 was considerably higher than for test 136. The high value was considered to be in error, since this stage catch contains the coarse particulate and most of the coarse particulate is expected to be removed by scrubbing. The high weight was probably due to some extraneous matter which was found on the impactor plate. Because the outlet impactor data agreed quite well for the two tests, with the exception of the two points which could reasonably be discarded, the data from test 136 was used to calculate the outlet weight distribution data for comparison with the inlet PLM data from test 135. This is presented in the text in Table 4-9.

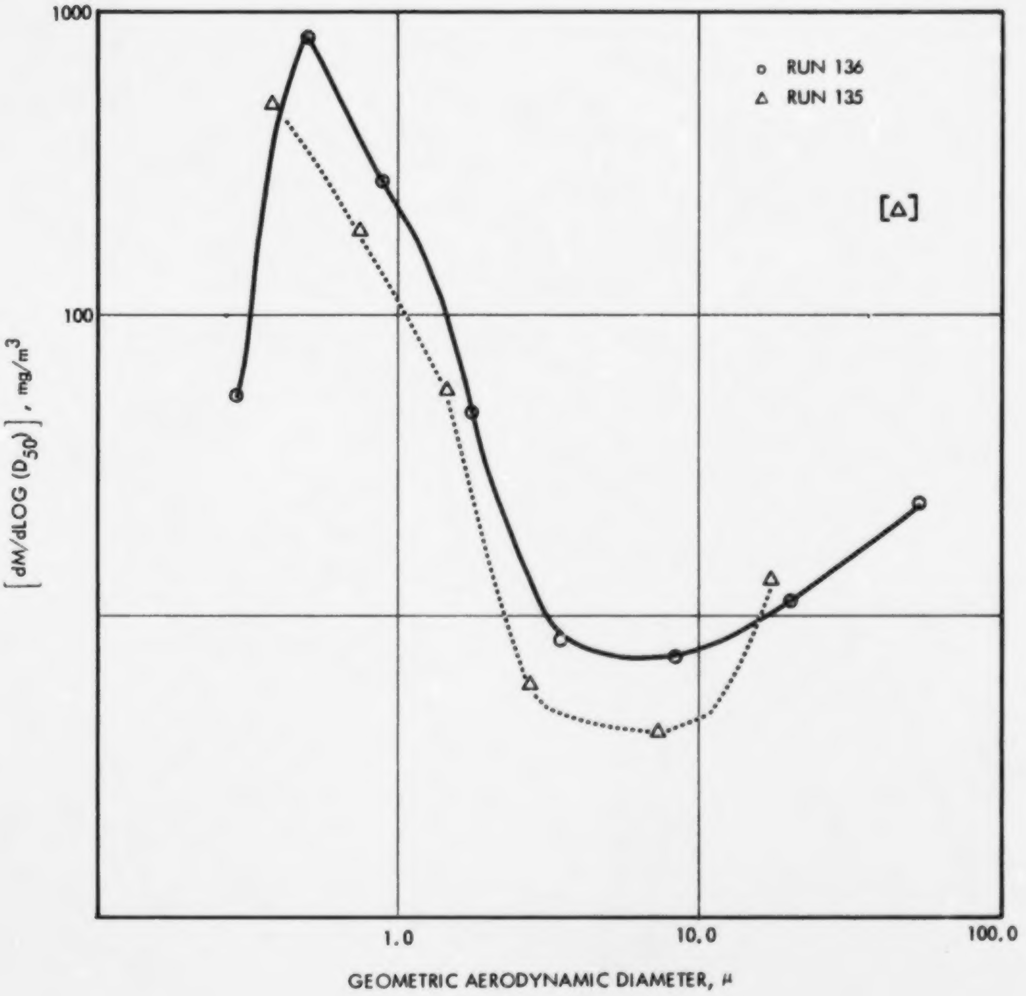

Figure C-24. Outlet MRI Weight Data for Runs 135 & 136

REFERENCES FOR APPENDIX C

C-1. Ensor, D.S., et al. Evaluation of a Particulate Scrubber on a Coal-Fired Utility Boiler. Prepared by Meteorology Research, Inc. for the U.S. Environmental Protection Agency. EPA 600/2-75-074. November 1975.